# 19 Sugars, Sugar Alcohols and Honey

## 19.1 Sugars, Sugar Alcohols and Sugar Products

### 19.1.1 Foreword

Only a few of the sugars occurring in nature are used extensively as sweeteners. Besides sucrose (saccharose), other important sugars are: glucose (starch sugar or starch syrup); invert sugar (equimolar mixture of glucose and fructose); maltose; lactose; and fructose. In addition, some other sugars and sugar alcohols (polyhydric alcohols) are used in diets or for some technical purposes. These include sorbitol, xylitol, mannitol, maltulose, isomaltulose, maltitol, isomaltitol, lactulose and lactitol. Some are used commonly in food and pharmaceutical industries, while applications for others are being developed. Food-grade oligosaccharides, which can be economically produced, are physiologically and technologically interesting. This group includes galacto-, fructo-, malto- and isomalto-oligosaccharides. Table 19.1 reviews relative sweetness, source and means of production, and Table 19.2 gives nutritional and physiological properties. Whether compounds will be successful as a sweetener depends on nutritional, physiological and processing properties, cariogenicity as compared to sucrose, economic impact, and the quality and intensity of the sweet taste.

### 19.1.2 Processing Properties

The potential of a compound for use as a sweetener depends upon its physical, processing and sensory properties. Important physical properties are solubility, viscosity of the solutions, and hygroscopicity. Figure 19.1 shows that the solubility of sugars and their alcohols in water is variable and affected to a great extent by temperature.

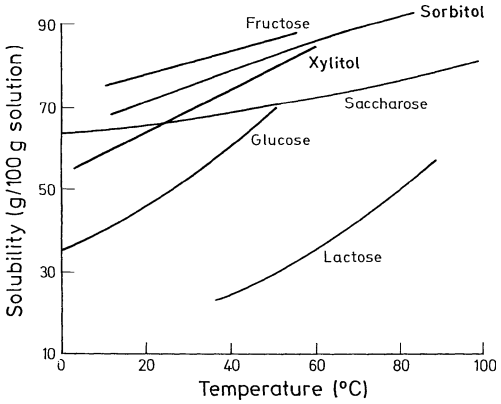



**Fig. 19.1.** Solubility of sugars and sugar alcohols in water (according to *Koivistoinen*, 1980)

There are similar temperature and concentration influences on the viscosity of aqueous solutions of many sugars and sugar alcohols. As an example, Fig. 19.2 shows viscosity curves for sucrose as a function of both temperature and concentration.

The viscosity of glucose syrup depends on its composition. It increases as the proportion of the high molecular weight carbohydrates increases (Fig. 19.3).

Figure 19.4 shows the water absorption characteristics of several sweeteners. Sorbitol and fructose are very hygroscopic, while other sugars absorb water only at higher relative humidities.

Chemical reactions of sugars were covered in detail in Chapter 4. Only those reactions important from a technological viewpoint will be emphasized here.

All sugars with free reducing groups are very reactive. In mildly acidic solutions monosaccharides are stable, while disaccharides hydrolyze to yield monosaccharides. Fructose is maximally stable at pH 3.3; glucose at pH 4.0. At lower pH's dehydration reactions prevail, while the *Lobry de Bruyn–van Ekenstein* rearrangement oc-

**Table 19.1.** Sweeteners of carbohydrate origin

| Name | Relative sweetness[a] | Starting material, applied process |
|---|---|---|
| Saccharose | 1.00 | Isolation from sugar beet and sugar cane |
| Glucose | 0.5–0.8 | Hydrolysis of starch with acids and/or enzymes (α-amylase + glucoamylase) |
| Fructose | 1.1–1.7 | a) Hydrolysis of saccharose, followed by separation of the hydrolysate by chromatography.<br>b) Hydrolysis of starch to glucose, followed by isomerization and separation by chromatography |
| Lactose | 0.2–0.6 | Isolation from whey |
| Mannitol | 0.4–0.5 | Hydrogenation of fructose |
| Sorbitol | 0.4–0.5 | Hydrogenation of glucose |
| Xylitol | 1.0 | Hydrogenation of xylose |
| Galactose | 0.3–0.5 | Hydrolysis of lactose, followed by separation of hydrolysate |
| Glucose syrup (starch syrup) | 0.3–0.5[b] | Hydrolysis of starch with acids and/or enzymes; hydrolysate composition is strongly affected by process parameters (percentage of glucose, maltose, maltotriose and higher oligosaccharides) |
| Maltose | 0.3–0.6 | Hydrolysis of starch |
| Maltose syrup | | As glucose syrup; process parameters adjusted for higher proportion of maltose in hydrolysate (amylase from *Aspergillus oryzae*) |
| Glucose/fructose syrup (isoglucose, high fructose syrup) | 0.8–0.9 | Isomerization of glucose to glucose/fructose mixture with glucose isomerase |
| Invert sugar | | Hydrolysis of saccharose |
| Hydrogenated glucose syrup | 0.3–0.8 | Hydrogenation of starch hydrolysate (glucose syrup); composition is highly dependent on starting material (content of sorbitol, maltitol and hydrogenated oligosaccharides) |
| Maltitol syrup | | Hydrogenation of maltose syrup |
| Galacto-oligosaccharides | 0.3–0.6 | Transgalactosylation of lactose by β-galactosidase (lactase) |
| Lactitol | 0.3 | Hydrogenation of lactose |
| Lactulose | ca. 0.6 | Alkaline isomerization of lactose |
| Lactosucrose | 0.3–0.6 | Fructose from sucrose is transferred to lactose by β-fructofuranosidase |
| Maltitol | ca. 0.9 | Hydrogenation of maltose |
| Isomaltitol | 0.5 | Hydrogenation of isomaltose |
| Fructo-oligosaccharides | 0.3–0.6 | Controlled enzymatic hydrolysis of inulin by inulase |
| Palatinose | 0.3–0.6 | Enzymatic isomerization of sucrose |
| Palatinose oligosaccharides | 0.3–0.6 | Intermolecular condensation of palatinose |
| Palatinit | 0.45 | Hydrogenation of palatinose |
| Glucosyl sucrose | 0.5 | Glucose from maltose is transferred to sucrose by cyclomaltodextrin-glucotransferase |
| Malto-oligosaccharides | 0.3–0.6 | a) Hydrolysis of the 1,6-α-glycosidic bonds in starch (debranching) by pullulanase;<br>b) controlled hydrolysis by α-amylase |
| Isomalto-oligosaccharides | 0.3–0.6 | a) Hydrolysis of starch by α- and β-amylase;<br>b) transglucosylation by α-glucosidase |
| Gentio-oligosaccharides | 0.3–0.6 | From glucose syrup by enzymatic transglucosylation |
| L-Sorbose | 0.6–0.8 | From glucose |
| Xylitol | 1.0 | Hydrogenation of xylose |
| Xylo-oligosaccharides | 0.3–0.6 | Controlled hydrolysis of xylan by endo-1,4-β-xylanase |

[a] Sweetness is related to saccharose sweetness (= 1); the values are affected by sweetener concentration.
[b] Sweetness value is strongly influenced by syrup composition.

**Table 19.2.** Nutritional/physiological properties of carbohydrate-derived sweeteners

| Sweetener | Resorption in metabolism | Utilization | Effect on blood sugar level and insulin secretion | Other properties |
|---|---|---|---|---|
| Sucrose | Effective after being hydrolyzed | Hydrolysis to fructose and glucose | Moderately high | Cariogenic |
| Glucose | Effective | Insulin-dependent in all tissues | High | Less cariogenic than sucrose |
| Fructose | Faster than by diffusion process | In liver to an extent of 80% | Low | Accelerates alcohol conversion in liver |
| Lactose | Effective after being hydrolyzed | Hydrolysis to glucose and galactose | High | Intolerance by humans lacking lactase enzyme; laxative effect |
| Sorbitol | Diffusion | Oxidation to fructose | Low | Slightly cariogenic and laxative |
| Mannitol | Diffusion | Partially utilized by liver | Low | Slightly cariogenic and laxative |
| Xylitol | Diffusion | Utilized preferentially by liver and red blood cells | Low | Not cariogenic, available data indicate an anticariogenic effect; mildly laxative |
| Hydrogenated glucose syrup | After hydrolysis glucose effective; sorbitol by diffusion | Variable depending on composition | Variable, composition dependent | Slightly cariogenic; mildly laxative |
| Arabinitol | Diffusion | Not metabolized by humans | None | Side effects unknown; probably laxative |
| Galactose | Effective | Isomerization to glucose | High | Forms cataracts in the eyes in feeding trials with rats; probably laxative |
| Isomaltitol | None | Probably not metabolized | None | Side effects unknown; strongly laxative |
| Lactitol | None | Partial hydrolysis to galactose and sorbitol | None | Side effects unknown; strongly laxative |
| Lactulose | None | No hydrolysis | None | Effects the N-balance; strongly laxative, bifidogenic |
| Maltitol | Effective as glucose after hydrolysis; sorbitol by diffusion | Hydrolysis to glucose and sorbitol | Probably slight | Side effects unknown; laxative |
| Maltose | Effective after hydrolysis | Hydrolysis to glucose | High | Cariogenic; intravenously given it appears to be utilized directly and, like glucose, it is insulin-dependent |
| L-Sorbose | Diffusion | Utilized preferentially by liver | Probably slight | Feeding trials with dogs revealed hemolytic anemia at a higher dosage; probably laxative |
| D-Xylose | Diffusion | Not metabolized by humans | None | Forms cataract in the eyes in feeding trials with rats; probably laxative |

**Table 19.2.** continued

| Sweetener | Resorption in metabolism | Utilization | Effect on blood sugar level and insulin secretion | Other properties |
|---|---|---|---|---|
| Palatinit | | Partial hydrolysis to glucose, sorbitol, and mannitol | Probably slight | Side effects unknown |
| Galacto-oligosaccharides | Active after hydrolysis | Partial hydrolysis | Moderate | Bifidogenic, slightly cariogenic |
| Lactosucrose | Active after hydrolysis | Partial hydrolysis | Moderate | Bifidogenic, slightly cariogenic |
| Fructo-oligosaccharides | Active after hydrolysis | Partial hydrolysis | Slight | |
| Glucosyl-sucrose | Active after hydrolysis | Partial hydrolysis | Slight | Slightly cariogenic |
| Malto-oligosaccharides | Active after hydrolysis | Hydrolysis in the small intestine | High | Reduction of undesirable bacteria in intestine |
| Isomalto-oligosaccharides | Active after hydrolysis | Slight hydrolysis | Low | Bifidogenic |
| Gentio-oligosaccharides | None | | None | Bifidogenic |
| Xylo-oligosaccharides | None | No change | None | Bifidogenic |

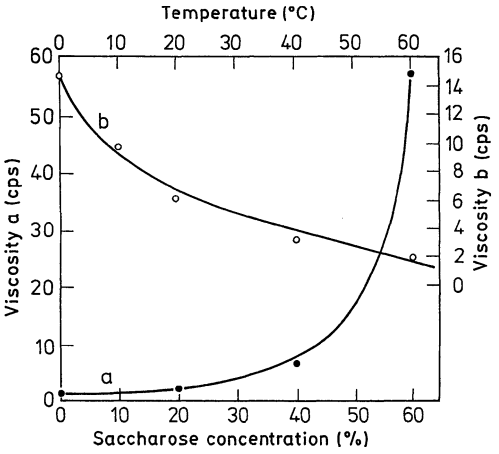



**Fig. 19.2.** Viscosity of aqueous saccharose solutions as a function of (a) saccharose concentration (20 °C) and temperature (40% saccharose) (according to *Shallenberger* and *Birch*, 1975)

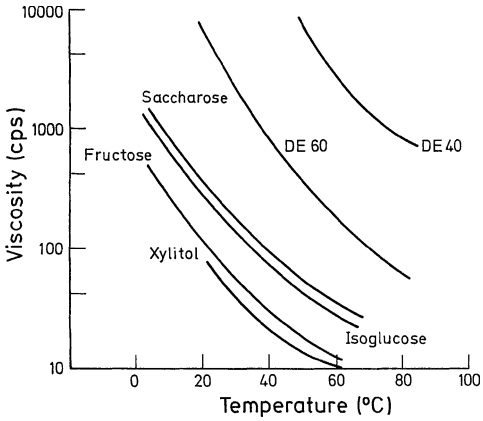



**Fig. 19.3.** Viscosity of some sugar solutions. Glucose syrup DE40: 78 weight-%; glucose syrup DE60: 77 weight-%; all other sugar solutions: 70 weight-% (according to *Koivistoinen*, 1980)

curs at higher pH's. Reducing sugars are unstable in mildly alkaline solutions, while nonreducing disaccharides, e. g., sucrose, have their stability maxima in this pH region.

The thermal stability of sugars is also quite variable. Sucrose and glucose can be heated in neutral solutions up to 100 °C, but fructose decomposes at temperatures as low at 60 °C.

Sugar alcohols are very stable in acidic or alkaline solutions. Relative taste intensity values for various sweeteners are found in Table 19.1. Taste intensity within a food can depend on a series of parameters, e. g., aroma, pH or food texture.

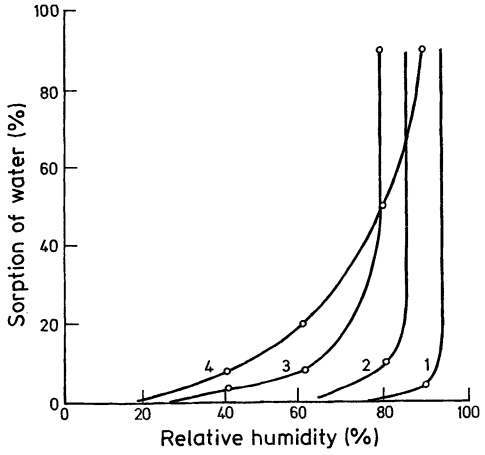



**Fig. 19.4.** Sorption of water by sugars at room temperature. *1* Saccharose, *2* xylitol, *3* fructose, *4* sorbitol (according to *Koivistoinen*, 1980)

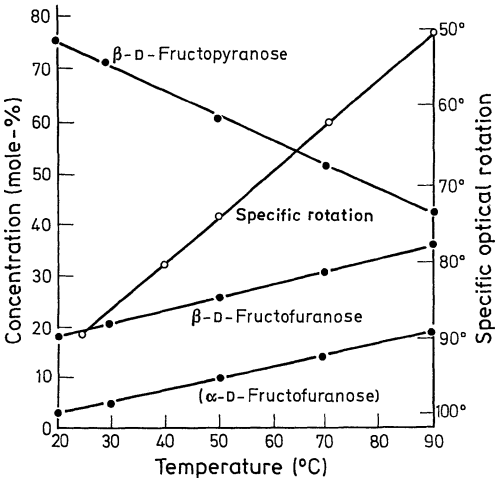



**Fig. 19.6.** Fructose mutarotation equilibrium as affected by temperature (according to *Shallenberger*, 1975)

Creams and gels with the same amounts of sweetener are often less sweet than the corresponding aqueous solutions. The sweet taste intensity may also depend on temperature (Fig. 19.5), an effect which is particularly pronounced with fructose – hot fructose solutions are less sweet than cold ones. The cause of such effects is the mass equilibrium of sugar isomers in solution. At higher temperatures the concentration of the very sweet β-D-fructopyranose drops in favor of both the less sweet α-D-fructofuranose and the β-D-fructofuranose (Fig. 19.6). Such strong shifts in isomer concentrations do not occur with glucose, hence its sweet taste intensity is relatively unchanged in the range of 5–50 °C.

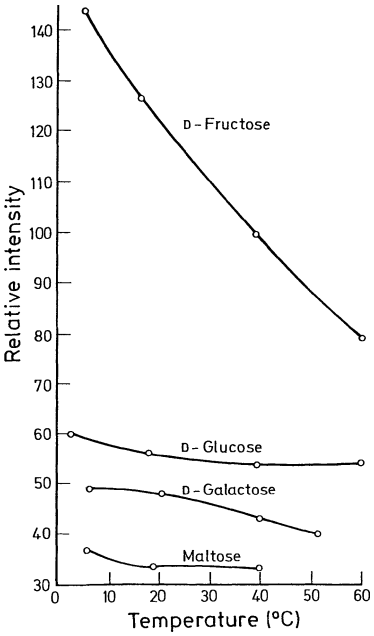



**Fig. 19.5.** Sugar sweetness intensity versus temperature. At all temperatures the saccharose taste intensity is 100 (according to *Shallenberger*, 1975)

### 19.1.3 Nutritional/Physiological Properties

#### 19.1.3.1 Metabolism

The role of carbohydrates in metabolism is primarily determined by the ability of disaccharides to be hydrolyzed in the gastrointestinal tract and by the mechanisms of monosaccharide absorption.

The human organism hydrolyzes sucrose, lactose and oligosaccharides of the maltose and isomaltose type. The enzyme lactase, which is responsible for lactose hydrolysis, is lacking in some adults. Glucose and galactose are actively transported, while all other monosaccharides are transported only by diffusion. Sugar phospho-

rylation occurs preferentially in the liver. All monosaccharides which are metabolized can be interconverted. Sugar alcohols are oxidized: sorbitol → fructose, xylitol → xylulose. However, only glucose can enter the insulin-regulated and -dependent energy metabolism and be utilized by all tissues. Galactose is rapidly transformed into glucose and is therefore nutritionally equal to glucose. Oral intake of glucose and galactose causes a rapid increase in blood sugar levels and, as a consequence, insulin secretion. All other monosaccharides are primarily metabolized by the liver and do not directly affect glucose status or insulin release.

#### 19.1.3.2 Glycemic Index

The glycemic index (GI) was introduced for the quantification of the blood sugar raising effect of carbohydrates. To determine the GI, the duration and the extent of the increase in blood sugar after consumption of 50 g of carbohydrate from food are measured. The reference value is the increase in blood sugar after the intake of 50 g of glucose (GI = 100%). The GI of maltose (105) is higher, but the GI of sucrose (65), lactose (46) and fructose (23) is lower.
The glycemic load (GL) was introduced to take into account the quantity of food consumed. This value refers to the glycemic total load of a portion of food consumed. Results are to be found on the Internet. The consumer, especially diabetics, should favour carbohydrate-containing foods with a low GL value.

#### 19.1.3.3 Functional Food

Some oligosaccharides are bifidogenic (Table 19.2) because they enter the large intestine and promote the growth of Bifidobacteria there. This is desirable because potential pathogenic microorganisms (*Enterobacteriaceae, Clostridia*), which cannot metabolize these oligosaccharides, are simultaneously repressed. Apart from vitamins, natural substances with an antioxidative effect, minerals and trace elements, *n*-3 and *n*-6 polyunsaturated fatty acids and phytosterols (cf. 3.8.2.3), bifidogenic oligosaccharides belong to the components of functional foods. These are products which not only have a pure nutritional value, but also offer a physiological advantage which is supposed to promote health. This definition is naturally unclear because it includes many traditional foods, such as water, which prevents the formation of kidney and bladder stones. Functional foods contain, e. g., substances which inhibit cancer or reduce cholesterol, protect against infections of the gastro-intestinal tract, reduce blood pressure etc. Whether a product actually meets these requirements must be properly checked so that the consumer is not disappointed (Katan and DeRoos, 2004). Bifidogenic oligosaccharides and inulin (cf. 4.4.4.22) belong to the group of *prebiotics*. These are indigestible substances which promote the growth in the intestine of bifidobacteria or possibly also other microorganisms. In this way, they should have positive effects on health (cf. Probiotocs, 10.2.1.2).

### 19.1.4 Individual Sugars and Sugar Alcohols

#### 19.1.4.1 Sucrose (Beet Sugar, Cane Sugar)

##### 19.1.4.1.1 General Outline

Sucrose is widely distributed in nature, particularly in green plants, leaves and stalks (sugar cane 12−26%; sweet corn 12−17%; sugar millet 7−15%; palm sap 3−6%); in fruits and seeds (stone fruits, such as peaches; core fruits, such as sweet apples; pumpkins; carobs or St. John's bread; pineapples, coconuts; walnuts; chestnuts); and in roots and rhizomes (sweet potatoes 2−3%; peanuts 4−12%; onions 10−11%; beet roots and selected breeding forms 3−20%). The two most important sources for sucrose production are sugar cane (*Saccharum officinarum*) and sugar beet (*Beta vulgaris ssp. vulgaris* var. *altissima*). Cane sugar and beet sugar are distingushed by the spectrum of accompanying substances and by the $^{13}C/^{12}C$ ratio, which can be used for identification (cf. 18.4.3).
Sucrose is the most economically significant sugar and is produced industrially in the largest quantity. Table 19.3 provides an overview of the annual world production of beet and cane sugar. Table 19.4 lists the main producers and Table 19.5 gives the sugar consumption in some countries.

**Table 19.3.** World production of sugar (beet/cane)

| Year | Total production $10^6$ t | Cane sugar % |
|---|---|---|
| 1900/01 | 11.3 | 47.0 |
| 1920/21 | 16.4 | 70.5 |
| 1940/41 | 30.9 | 62.3 |
| 1960/61 | 61.1 | 60.3 |
| 1965/66 | 71.1 | 61.8 |
| 1970/71 | 82.3 | 64.2 |
| 1975/76 | 92.2 | 64.6 |
| 1980/81 | 98.4 | 66.6 |
| 1981/82 | 108.5 | 66.2 |
| 1982/83 | 98.6 | 62.9 |
| 1996 | 124 | |
| 1999 | 133 | |
| 2003/04 | 146 | 76.0 |

Honey is the oldest known sweetener and has relatively recently been displaced by cane sugar. Cane sugar was brought to Europe from Persia by the Arabs. After the Crusades, it was imported by Cyprus and Venice and, later, primarily by Holland, from Cuba, Mexico, Peru and Brazil.

In 1747 *Marggraf* discovered sucrose in beets and in 1802 *Achard* was the first to produce sucrose commercially from sugar beets. The

**Table 19.5.** Sugar consumption in selected countries in 2003

| Country | Consumption[a] |
|---|---|
| Brazil | 53.4 |
| Mexico | 52 |
| Australia | 50.5 |
| Germany | 36.2 |
| EU-15 | 34.2 |
| Former USSR | 33.2 |
| USA | 27.9 |
| Turkey | 22.4 |
| India | 16.7 |
| China | 7.8 |

[a] kg/year and head.

**Table 19.4.** Production of sugar beet, sugar cane and saccharose in 2006 (1000 t)

| Continent | Sugar cane | Sugar beet | Saccharose[a] |
|---|---|---|---|
| World | 1,392,365 | 256,407 | 2264 |
| Africa | 92,540 | 5682 | 16 |
| America, Central | 91,417 | – | 5 |
| America, North | 26,835 | 29,751 | 11,000 |
| America, South and Caribbean | 661,456 | 2225 | 1732 |
| Asia | 569,852 | 36,224 | 365 |
| Europe | 60 | 182,525 | 128 |
| Oceania | 41,622 | – | 12 |

| Country | Sugar cane | Country | Sugar beet | Country | Saccharose[a] |
|---|---|---|---|---|---|
| Brazil | 455,291 | Russian Fed. | 30,861 | Colombia | 1722 |
| India | 281,170 | France | 29,879 | Indonesia | 205 |
| China | 100,684 | USA | 28,880 | China | 46 |
| Mexico | 50,597 | Ukraine | 22,421 | Bangladesh | 36 |
| Thailand | 47,658 | Germany | 20,647 | Myanmar | 31 |
| Pakistan | 44,666 | Turkey | 14,452 | UK | 27 |
| Colombia | 39,849 | Poland | 11,475 | Lithuania | 26 |
| Australia | 38,169 | Italy | 10,641 | Belgium | 22 |
| Indonesia | 30,150 | China | 10,536 | Korea, Rep. | 18 |
| USA | 26,835 | UK | 7150 | Thailand | 18 |
| $\sum$ (%)[b] | 78 | Spain | 6045 | $\sum$ (%)[b] | 75 |
| | | $\sum$ (%)[b] | 75 | | |

[a] As raw (centrifuged) sugar.
[b] World production = 100%.

new sugar source had great economic impact; the more so when sucrose accumulation in the beets was increased by selection and breeding.

#### 19.1.4.1.2 Production of Beet Sugar

The isolation of beet sugar will be described first because the processes used in material preparation and sugar separation have been developed to perfection. These processes were later transferred to the production of cane sugar from the clear juice concentration stage onwards. In fact, cane sugar was processed fairly primitively for a long time.

Prolonged selection efforts have led to sugar beets which reach their maximum sucrose content of 15–20% in the middle of October. The average for 1980–85 in FR Germany was 16.3%. The early yield achieved by *Achard* of 4.5 kg/100 kg beets has been increased to about 14 kg. Currently, beet varieties have a high sugar content and small amounts of nonsugar substances. Anatomically they have a favorable shape, i. e. are small and slim with a smooth surface, and have a firm texture. Since the sugar accumulation in beets peaks in October and since sugar decomposition due to respiration occurs during subsequent storage of beets, they are rapidly processed from the end of September to the middle of December.

The beet sugar extract contains about 17% sucrose, 0.5% inorganic and 1.4% organic nonsucrose matter. Invert sugar and raffinose content is 0.1% (in molasses this may be as high as 2%). The trisaccharide kestose (cf. 4.3.2), which is present in the extract, is an artifact generated in the course of beet processing. In addition to pectic substances, beet extract contains saponins which are responsible for foaming of the extract and binding with sugars. N-containing, nonsugar constituents of particular importance are proteins, free amino acids, and their amides, (e. g., glutamine) and glycine betaine ("betaine"). These constituents are 0.3% of beets and about 5% of molasses. Beet ash averages 28% potassium, 4% sodium, 5% calcium and 13% phosphoric acid, and contains numerous trace elements. The nonsugar constituents of the sugar extract also include steam-distillable odorous compounds, phenolic acids, e. g., ferulic acid, and numerous beet enzymes which are extensively inactivated during extract processing. These enzymes, e. g., polyphenol oxidase, can induce darkening through melanin build-up, with the color being transferred during beet extraction into the raw sugar extract.

Beet processing involves the following steps:

- *Flushing and cleaning* in flushing chutes and whirlwashers.
- *Slicing* with machines into thin shreds (cossettes) with the shape of "shoestrings" 2–3 mm thick and 4–7 mm wide.
- *Extraction* by leaching of beet slices. The extraction water is adjusted to pH 5.6−5.8 and to 30−60 °dH with $CaCl_2$ or $CaSO_4$ to stabilize the skeletal substances of the slices in the following pressing step. To denature the cells, the slices are first heated to 70−78 °C for ca. 5 minutes (preliminary scalding) and then extracted at 69−73 °C for 70 to 85 minutes. To eliminate thermophilic microorganisms in the extraction system, 30−40% formaldehyde solution is intermittently added to the raw material at intervals of 8−24 hours in amounts of 0.5−1% of the raw juice accumulating hourly. This was once performed in a so-called diffusion battery of 12–14 bottom sievo-equipped cylindrical containers (diffusers) connected in series and operating discontinuously on a countercurrent principle. Today this battery operation has been replaced to a great extent by a continuous and automatically operated extraction tower into which the shreds are introduced at the bottom while the extraction fluid flows from the top. The extracted shreds (pulp) are discharged at the top. The pulp contains residual sugar of approx. 0.2% of the beet dry weight.

  The pulp is pressed, dried on band dryers, and pelleted. It serves as cattle feed. Before drying, 2–3% of molasses and, for nitrogen enrichment, urea is sometimes added.
- *Raw Sugar Extract Purification* (liming and carbonatation). Juice purification results in the removal of 30−40% of the nonsugar substances and has the following objectives:
  - Elimination of fibers and cell residue
  - Precipitation of proteins and polysaccharides (pectins, arabans, galactans)
  - Precipitation of inorganic (phosphate, sulfate) and organic anions (citrate, malate,

oxalate) as calcium salts and precipitation of magnesium ions as $Mg(OH)_2$
- Degradation of reducing sugar (invert sugar, galactose) and, therefore, suppression of the *Maillard* reaction during evaporation
- Conversion of glutamine to pyrrolidone carboxylic acid and asparagine to aspartic acid. However, these reactions proceed only partially under the usual conditions of juice purification.
- Adsorption of pigments on the $CaCO_3$ formed.

Moreover, the sludge formed must be easily settleable and filtrable.

The raw juice from the extraction tower is turbid and greyish black in color due to the enzymatic oxidation of phenols, especially of tyrosine, and to the presence of phenoliron complexes. The raw juice has a pH of 6.2 and contains on an average 15% of solids, of which sucrose accounts for 13.5%. It is first mechanically filtered and then treated with lime milk in two steps (preliming and main liming). Preliming is generally conducted at 60−70 °C up to a pH of 10.8−11.9 with a residence time of at least 20 minutes. Main liming is conducted at 80−85 °C with a residence time of ca. 30 minutes up to a total CaO content of 2−2.5% in the juice. A number of organic acids and phosphate are precipitated as calcium salts and colloids flocculate.

In order to remove excess calcium, decompose the calcium saccharate ($C_{12}H_{22}O_{11} \times 3CaO$) formed, and transform the precipitated turbidity-causing solids into a more filtrable form, the solution is quickly gassed with an amount of carbon dioxide required for the formation of calcium carbonate. Carbonatation is also performed in two steps. In the 1st. carbonatation step at 85 °C, the pH is adjusted to 10.8−11.9. The sludge formed (50−60 g solids/l) is separated at 90−95 °C via decanters and filters and washed on the filters up to a residual sugar content of 0.1−1%. In the 2nd. carbonatation step, a pH of 8.9−9.2 is reached at 94−98 °C. The small amount of sludge (1−3 g solids/l) is filtered off. To lighten and stabilize the color during subsequent evaporation, 50 g/m$^3$ of $SO_2$ (sulfitation) are frequently added to the thin syrup (juice). Subsequently, the solution is again clarified by filtration, finally producing a clear light-colored thin juice with a solids content of 15 to 18%.

Apart from the classical juice purification processes, different variants are known, which have both advantages and disadvantages. They yield carbonatation juices that can be decanted and filtered more easily. However, these juices are frequently more thermolabile because of incomplete destruction of invert sugar and consequently discolor on evaporation.

Ion exchangers have become important in juice purification. They soften the thin syrup and prevent the formation of hardness scale on the evaporator coils. The substitution of alkaline earth ions (Mg) for the alkali ions is beneficial because it decreases the sugar lost in the molasses by ca. 30% due to the stronger hydration of the alkaline earth ions. Bleaching of thin syrup is possible with activated carbon or with large-pore ion exchangers, which bind the pigments mainly by adsorption.

Extensive elimination (ca. 85%) of nonsugar substances with a corresponding increase in the sugar yield can be achieved by a combination of cation exchangers ($H^{\ominus}$ form) and anion exchangers ($OH^{\ominus}$ form) (complete desalting). To suppress inversion during the temporary pH drop, the operation must be conducted at low temperatures (14 °C). Higher temperatures (60 °C) can be used if the cations are first replaced by ammonium ions which are then eliminated as ammonia with the help of an anion exchanger or fixed on a mixed-bed exchanger. In comparison with the lime-carbon dioxide treatment, however, complete desalting has not yet gained acceptance.

- *Evaporation of the thin syrup* (15−18% solids) is achieved in multiple-stage evaporators (falling film evaporators, natural or forced circulation evaporators). Mildly alkaline conditions (pH 9) are maintained to prevent sucrose inversion. The boiling temperatures decrease in the range of 130−90 °C. The resultant thick syrup (yield of 25−30 kg/100 kg beet) is once more filtered. The syrup contains 68−72% solids and sucrose content is 61−67%. The raw, thin and thick syrups have purity quotients of approx. 89, 92 and 93, respectively, i. e. the percentage sucrose on a dry matter basis.

  During evaporation, calcium salts precipitate, glutamine still present is converted to pyrrolidone carboxylic acid with lowering of the pH,

alkaline degradation of sugar occurs to a small extent, and darkening of the syrup occurs due to *Maillard* reaction and caramelization, depending on the process management (temperature, residence time in the evaporation stages).

- *Crystallization*. Multistage crystallization can be used to isolate 85–90% of the sucrose contained in the thick syrup. The remaining sucrose and practically all the non-sugar substances are found in the last mother liquor called molasses. The crystallization process is predominantly a discontinuous operation. However, efforts are being made to introduce a continuous process (evaporative crystallization and centrifugation).

  The thick syrup is evaporated in a boiling apparatus at 0.2–0.3 bar and 65–80 °C until slight supersaturation is achieved (evaporative crystallization). Crystallization is then initiated by seeding, e. g., by adding a dispersion of sucrose crystals (0.5–30 μm) in isopropanol. The mixture is further boiled until the crystals acquire the required size. In this process, the formation of both new crystals and crystal conglomerates is to be carefully prevented by intensive circulation (steam generation, stirring). The crystal paste (magma) with a crystal content of 50–60% is discharged into mashers for homogenization with constant stirring at a constant temperature.

  A further crystallization occurs in part on very slow cooling to 35–40 °C (cooling crystallization). In this process, the viscosity of the mash must be maintained constant by the addition of water or mother syrup. Today, cooling crystallization is generally used only for after-product magma, but it will be of importance for raw sugar and white sugar.

  Subsequently, the crystalline sugar from the mashers or massecuite is centrifuged in centrifugal baskets, eliminating the mother liquor called green syrup, which is returned to the process. The sugar (with the exception of raw sugar) is then freed from adhering syrup by washing with hot water and steam in the centrifuge. The resulting sugar solution (wash syrup) is fed back to the crystallization process. The presence of higher concentrations of raffinose in the magma (>1%, based on dry matter) reduces the rate of crystallization of sucrose and produces needle-shaped crystals. For this reason, raffinose is cleaved by α-galactosidase.

  In this manner, thick syrup can be processed into raw sugar or consumer sugar (white sugar and refined sugar), depending on the process operation. The different crystallization schemes are simplified in Fig. 19.7. Raw sugar contains 1–1.2% of organic and 0.8–1% of inorganic nonsugar substances

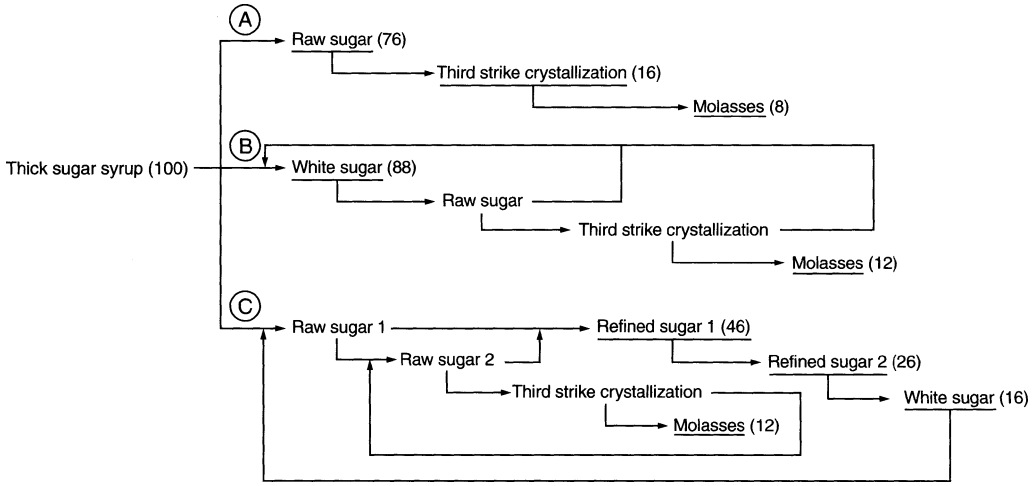



**Fig. 19.7.** Crystallization scheme for the production of A) raw sugar, B) white sugar, and C) refined sugar. The yields of sucrose (%), based on the amount of sucrose added with the thick syrup, are given in brackets behind the final products (*underlined*)

and 1–2% of water. It is light yellow to dark brown in color due to the adhering syrup. Like the after-product sugar (3–4% of organic and 1.5–2.5% of inorganic nonsugar substances and 2–3% of water) obtained in the last crystallization stage, raw sugar is generally not suitable for direct use. It is processed to consumer sugar in refineries.

In the refinery, the sugar is mashed into a magma with a suitable syrup, centrifuged, and washed with water and steam (affination). Thus, it directly yields a consumer sugar called affinated sugar. Another possibility is to dissolve the sugar and feed the resulting syrup (liquor) to a crystallization process which then yields refined sugar, a consumer sugar of the highest quality.

A simplified crystallization scheme for the production of white sugar is presented in Fig. 19.8. After affination and dissolving, the raw sugar and after-product sugar accumulating in the course of the process are boiled down together with the thick syrup, and the main part of the sugar finally crystallizes out of the supersaturated solution as white sugar. Centrifugation at 40–45 °C yields not only crystals of 2–4 mm (first-product sugar), but also centrifugal syrup (green syrup) which is subjected to two further crystallization steps. The last discharge, a highly viscous brown syrup, is molasses. In the processing of thick syrup to refined sugar, first raw sugar is isolated exclusively. It is then dissolved and fed back into the crystallization process. In this way, the process is independent of variations in the quality of the thick syrup.

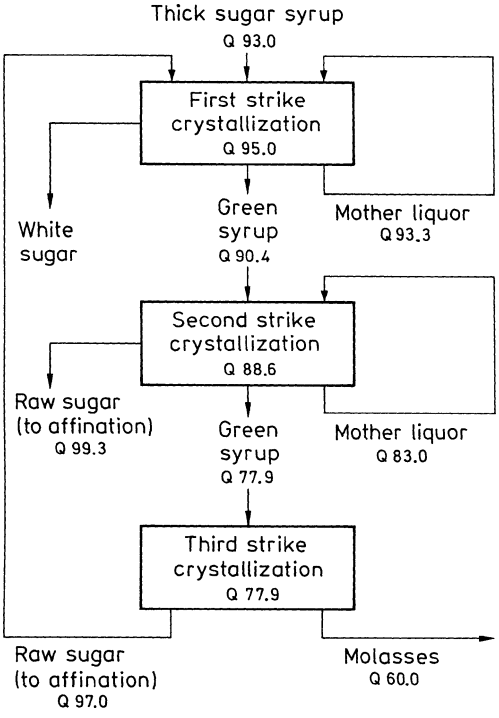



**Fig. 19.8.** White sugar evaporation and crystallization. Quotient Q: % saccharose in dry matter

**Table 19.6.** Production losses[a] during saccharose recovery from sugar beet

| Processing step | 1950 | 1974 |
|---|---|---|
| Beet slice extraction | 0.4–0.5 | 0.15–0.25 |
| Sugar extract purification | 0.1–0.2 | 0.02–0.05 |
| Other steps | 0.6–0.8 | 0.25–0.90 |
| Total process | 1.1–1.5 | 0.42–0.60 |

[a] Sugar amount in % based on the processed beet weight.

Processing losses in sucrose recovery from beets in 1974 were 0.4–0.9% (sugar determined polarimetrically; and based on processed beet weight) and, when compared to 1950, represent a significant improvement of the sucrose yield (Table 19.6). This technological progress is also reflected in a rise of work productivity (work min/t beets), which was 130–150 in 1950 but only 12–30 in 1974.

#### 19.1.4.1.3 Production of Cane Sugar

Sugar cane processing starts with squeezing out the sweet sap from thoroughly washed cane. For this purpose, the cane moves to a shredding machine where knives shred the stalks and then moves to crushing machines where a series of revolving heavy steel rollers squeeze the cane under high pressure. After the first roller, more than 60% of the cane weight is removed in the form of sap which contains 70% or more of the cane sucrose content. Repeated squeezing provides a sucrose yield of 93–97.5%. The squeezing may be combined with extraction by mixing the "bagasse" (the pressed cane) with hot

water or dilute hot cane juice, followed by a final pressing. The experience gained in continuous thin beet syrup production is applied to sugar cane production, with a resultant energy saving and a rise in sugar yields.
Clarification and neutralization of the mildly acidic, raw extract (pH 4.8−5.0) is done by treatment with lime or lime and carbon dioxide. Further processing of the clarified pure syrup parallels that of sugar beet processing. The yield of raw cane sugar is 6–11% of the cane weight.
The "bagasse" is used as fuel, made into wallboard or used as insulation.

#### 19.1.4.1.4 Other Sources for Sucrose Production

Some plants other than sugar beet or sugar cane can serve as sources of sucrose:

*Date Sugar* is obtained from the sweet, fleshy fruit of the date palm (Algeria, Iraq), which contains up to 81% sucrose in its solids.

*Palm Sugar* originates from various palm species, e. g., palmyra, saga or Toddy palm, coconut and Nipa palm grown in India, Sri Lanka, Malaysia and the Philippines, respectively.

*Maple Sugar* is obtained from the maple tree (*Acer saccharum*), found solely in North America (USA and Canada) and Japan. The sap, which drips from holes drilled in the maple tree trunk, flows down metal spiles into metal pails. This sap contains about 5% sucrose, minute amounts of raffinose and several other oligosaccharides of unknown structures. It is marketed in concentrated form either as maple syrup or as maple sugar. Aroma substances are important constituents of these products. The syrup also contains various acids, e. g., citric, malic, fumaric, glycolic and succinic acids. The main component of maple sugar is sucrose (88–99% of the total solids). Aroma constituents include vanillin, syringic aldehyde, dihydroconiferyl alcohol, vanilloyl methyl ketone and furfural.

*Sorghum Sugar.* Sugar sorghum (*Sorghum dochna*) stalks contain 12% sucrose. This source was important earlier in the USA. Sugar sorghum is processed into sorghum syrup on a small scale on individual farms in the Midwestern United States.

#### 19.1.4.1.5 Packaging and Storage

Sucrose is packaged in paper, jute or linen sacks, in cardboard boxes, paper bags or cones, in glass containers and in polyethylene foils; the latter serving as lining in paper, jute or wooden containers.
Sugar is stored at a relative humidity of 65−70% in loose form in bins or by stacking the paper or jute sacks. The unbagged, loose or bulk sugar is distributed to industry and wholesalers in bins on trucks or rail freight cars.

#### 19.1.4.1.6 Types of Sugar

Sucrose is known under many trade and popular names. These may be related to its purity grade (raffinade, white, consumer's berry, raw or yellow sugar), to its extent of granulation or crystal size (icing, crystal, berry and candy sugar, and cube and cone sugar) and to its use (canning, confectionery or soft drink sugar). Liquid sugar is a sucrose solution in water with at least 62% solids (of which a maximum of 3% is invert sugar). The invert sugar content is high in liquid invert sugars and invert sugar syrups. Such solutions are easily stored, handled and transported. They are dosed by pumps and are widely used by the beverage industry (soft drinks and spirits), the canning industry and ice cream makers, confectionery and baking industries, and in production of jams, jellies and marmalades. Use of liquid sugar avoids the additional crystallization steps of sugar processing and problems associated with packaging of sugar.
Criteria for the analytical determination of sugars are: (a) color; (b) color extinction coefficient (absorbance) of a 50% sugar solution, expressed in ICUMSA-units; (c) ash content determined from conductivity measurements of a 28% aqueous sugar solutions; (d) moisture content; (e) optical rotation; and (f) criteria based on the content of invert sugar.

#### 19.1.4.1.7 Composition of some Sugar Types

The chemical composition of a given type of sugar depends on the extent of sugar raffination. A raffinade, as mentioned above, consists of

practically 100% sucrose. Washed raw beet sugar has about 96% sucrose, <1.4% moisture, 0.9% ash and 1.5% nonsugar organic substances. Berry sugar consists of 98.8% sucrose, 0.70% moisture, 0.20% ash and 0.29% nonsugar organic substances. The presence of raffinose, a trisaccharide, is detected by high optical rotation readings or by the presence of needle- or spearlike crystals.

19.1.4.1.8 Molasses

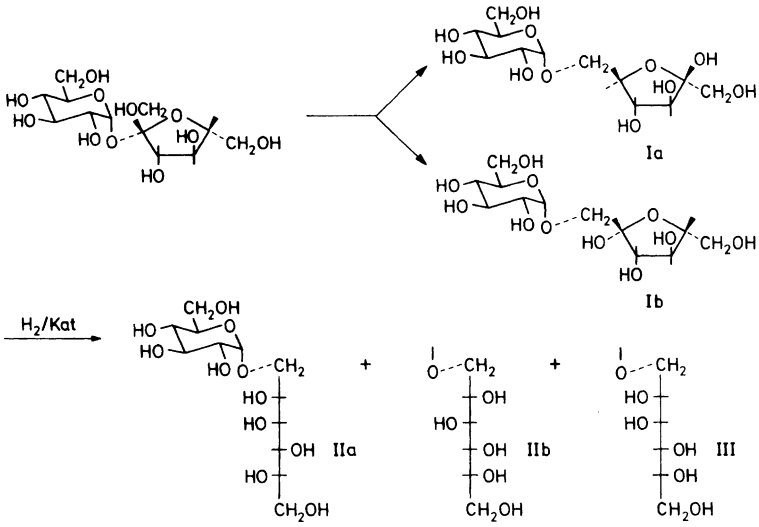
The molasses obtained after sugar beet processing contains about 60% sucrose and 40% other components (both on dry basis). The nonsucrose substances, expressed as percent weight of molasses, include: 10% inorganic salts, especially those of potassium; raffinose (about 1.2%); the trisaccharide kestose, an artifact of processing; organic acids (formic, acetic, propionic, butyric and valeric); and N-containing compounds (amino acids, betaine, etc.). The main amino acids are glutamic acid and its derivative, pyrrolidone carboxylic acid. Molasses is used in the production of baker's yeast; in fermentation technology for production of ethanol and citric, lactic and gluconic acids, as well as glycerol, butanol and acetone; as an ingredient of mixed feeds; or in the production of amino acids.

The residual molasses after cane sugar processing contains about 4% invert sugar, 30–40% sucrose, 10–25% reducing substances, a very low amount of raffinose and no betaine, but unlike beet molasses, contains about 5% aconitic acid. Cane sugar molasses is fermented to provide arrack and rum.

### 19.1.4.2 Sugars Produced from Sucrose

Hydrolysis of sucrose with acids, or enzymes (invertase or saccharase) results in invert sugar which, after chromatographic separation, can provide *glucose* and *fructose*. Invert sugar syrup is a commercially available liquid sugar. Invert sugar also serves as a raw material for production of sorbitol and mannitol. Isomerization of sucrose with isomaltulose synthase (EC 5.4.99.11) gives isomaltulose. Apart from 6-O-α-glucopyranosidofructose (palatinose, Ia, Formula 19.1), 1-O-α-glucopyranosidofructose (Ib) is also formed, the ratio depending on the reaction conditions. The process is operated continuously with the immobilized enzyme. The fructose component of palatinose is present as furanose, the anomer ratio being $\alpha/\beta = 0.25$ (34 °C). The sweetening strength is 0.4, based on a 10% sucrose solution. Palatinose is not cleaved by human mouth flora; it undergoes delayed cleavage by the glucosidases in the wall of the small intestines.

Catalytic hydrogenation yields isomaltol (palatinit), a mixture of the disaccharide alcohols




(19.1)

6-O-α-D-glucopyranosidosorbitol (IIa, Formula 19.1), 1-O-α-D-glucopyranosidosorbitol (IIb) (isomaltitol), and 1-O-α-D-glucopyranosidomannitol (III).

This mixture of sugar alcohols can be separated by fractional crystallization. Palatinit is a sugar substitute.

Isomalto-oligosaccharides [α-D-Glu-(1 → 6)-]$_n$, $n = 2 - 5$, produced by the intermolecular condensation of palatinose, can pass through the small intestine.

Enzymatic isomerization of sucrose with the help of *Leuconostoc mesenteroides* gives an α-D-glucopyranosido (1 → 5)-D-fructopyranose called *leucrose*. This sugar is fully metabolized but is non-cariogenic.

The transfer of glucose residues from maltose or soluble starch to sucrose with the help of a cyclodextrin glucosyltransferase gives mixtures of oligosaccharides [α-D-Glu-(1 → 4)-α-D-Glu-(1 → 2)-β-D-Fru], which are called glucosyl sucrose, and are only slightly cariogenic. The transfer of fructose residues to sucrose catalyzed by a fructosyltransferase gives fructo-oligosaccharides of the general formula α-D-Glu-(1 → 2)-[β-D-Fru-(1 → 2)-]$_n$ with $n = 2 - 4$, β-D-Fru-(1 → 2)-[β-D-Fru-(1 → 2)-]$_n$ with $n = 1 - 9$ and α-D-Glu-(1 → 2)-[β-D-Fru-(1 → 2)-]$_n$ with $n = 1-9$. Alternatively, the controlled hydrolysis of inulin is used in the production of fructo-oligosaccharides.

### 19.1.4.3 Starch Degradation Products

#### 19.1.4.3.1 General Outline

In principle, either starch or cellulose could be used as a source for saccharification, but only starch hydrolysis is currently of economic importance. Most of the enzymes used for this purpose are derived from genetically modified microorganisms.

#### 19.1.4.3.2 Starch Syrup (Glucose or Maltose Syrup)

Starch saccharification is achieved by either acidic or enzymatic hydrolysis. Controlled processing conditions yield products of widely different compositions to suit the diversified fields of application. Acid hydrolysis is conducted with hydrochloric acid or sulfuric acid, mainly in a continuous process, and yields glucose syrups with dextrose equivalents (DE value) between 20 and 68. The composition is constant for each DE value (Fig. 19.9).

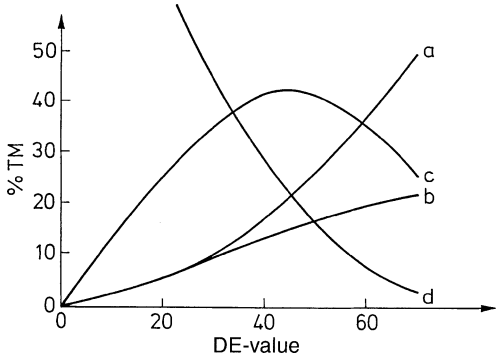



**Fig. 19.9.** Composition of starch syrups (acid hydrolysis). *a* Glucose, *b* maltose (disaccharide), *c* oligosaccharide (degree of polymerization DP = 3–7), *d* higher saccharides

The raw juice is neutralized and passes through various purification steps. Proteins and lipids from starch flocculate at a suitable pH value and are separated as sludge. Pigments are eliminated with activated carbon and minerals with ion exchangers. The purified juice is evaporated under vacuum (falling-film evaporator) up to a solids content of 70−85%.

During acid hydrolysis, a number of side reactions occur (cf. 4.2.4.3.1). Reversion products are formed in amounts of 5−6% of the glucose used. These are predominantly isomaltose (68−70%) and gentiobiose (17−18%), and, in addition, other di- and trisaccharides. Furthermore, degradation products of glucose are formed, e. g., 5-hydroxymethylfurfural and other compounds typical of caramelization and the *Maillard* reaction (cf. 4.2.4.4).

In enzymatic processes, α-amylases, β-amylases, glucoamylases, and pullulanases are used. First, starch liquefaction is conducted with acid, with α-amylase, or with a combination acid/enzyme process.

The enzyme most commonly used is α-amylase isolated from, for example, *Bacillus subtilis* or *B. licheniformis*. Optimal pH and temperature

are 6.5 and 70–90 °C, respectively. The enzyme from *B. licheniformis* is active even at 110 °C. Hydrolysis can be carried out to obtain a product consisting mostly of maltose and, in addition, maltotriose and small amounts of glucose. When, for instance, starch is subjected to combined degradation with bacterial α-amylase and β-amylase or fungal α-amylase, the product obtained has 5% of glucose, 55% of maltose, 15% of maltotriose, 5% of maltotetraose, and 20% of dextrins in the dry matter. Maltose contents of up to 95% (dry matter) can be attained by using pullulanases (cf. 2.7.2.2.4).

A suitable combination of enzymes gives rise to products that cannot be obtained by acid hydrolysis alone.

The extent of starch conversion into sugars is generally expressed as dextrose equivalents (DE value), i. e. the amount of reducing sugars produced, calculated as glucose (DE value: glucose = 100, starch = 0).

The sweet taste intensity of the starch hydrolysates depends on the degree of saccharification and ranges from 25–50% of that of sucrose. Table 19.7 provides data on some hydrolysis products. The wide range of starch syrups starts with those with a DE value of 10–20 (maltodextrins) and ends with those with a DE value of 96.

Starch syrups are used in sweet commodity products. They retard sucrose crystallization (hard caramel candies) and act as softening agents, as in soft caramel candies, fondants and chewing gum. They are also used in ice cream manufacturing, production of alcoholic beverages and soft drinks, canning and processing of fruits and in the baking industry.

#### 19.1.4.3.3 Dried Starch Syrup (Dried Glucose Syrup)

Dried starch syrups with a moisture content of 3–4% are produced by spray drying of starch hydrolysates. The products are readily soluble in water and dilute alcohol and are used, for example, in sausage production as a red color enhancer. The average composition of dried starch syrups is 50% dextrin, 30% maltose and 20% glucose.

#### 19.1.4.3.4 Glucose (Dextrose)

The raw source for glucose production is primarily starch isolated from corn, potatoes or wheat. The starch is first liquefied with thermostable α-amylases of microbial origin at 90 °C and pH 6.0 or by partial acid hydrolysis. The dextrins are then hydrolyzed by amyloglucosidase. The enzyme from *Aspergillus niger*, at pH 4.5 and 60 °C, provides a hydrolysate with 94–96% glucose. After a purification step, the hydrolysate is evaporated and crystallized. Glucose crystallizes as α-D-glucose monohydrate. Water-free α-D-glucose is obtainable from the monohydrate by drying in a stream of warm air or

**Table 19.7.** Average composition of starch hydrolysates[a]

| DE-Value[b] | Glucose | Maltose | Maltotriose | Higher oligosaccharides |
|---|---|---|---|---|
| *Acid hydrolysis* | | | | |
| 30 | 10 | 9 | 9 | 72 |
| 40 | 17 | 13 | 11 | 59 |
| 60 | 36 | 20 | 13 | 31 |
| *Enzymatic hydrolysis*[c] | | | | |
| 20 | 1 | 5 | 6 | 88 |
| 45 | 5 | 50 | 20 | 25 |
| 65 | 39 | 35 | 11 | 15 |
| 97 | 96 | 2 | – | 2 |

[a] All values expressed as % of starch hydrolysate (dry weight basis).
[b] cf. 19.1.4.3.2
[c] Occasionally it involves a combined acid/enzymatic hydrolysis.

by crystallization from ethanol, methanol or glacial acetic acid. Dextrose, due to its great and rapid resorption, is used as an invigorating and strengthening agent in many nourishing formulations and medicines. Like dried glucose syrup, crystalline dextrose is used as a red color enhancer of meat and frying sausages.

#### 19.1.4.3.5 Glucose-Fructose Syrup (High Fructose Corn Syrup, HFCS)

Glucose-fructose syrup is made by the enzymatic isomerization of glucose, which is derived from the process given in 19.1.4.3.4. The conversion occurs at pH 7.5 and 60 °C in a reactor with an isomerase of microbial origin fixed to a carrier. The pH is finally adjusted to 4–5 to avoid the *Maillard* reaction (browning). Since an isomerization of only 42% is achieved, the production of higher concentrations (e. g., 55%) requires the addition of fructose. The fructose is obtained from the syrup by chromatographic enrichment.As a result of a comparable sweetening strength, HFCS replaces sugar in many sweet foods. For example, HFCS accounts for 55% of the total sugar consumption in the USA and sugar for only 45%.

#### 19.1.4.3.6 Starch Syrup Derivatives

Hydrogenation of glucose syrups results in products which, since they are nonfermentable and are less cariogenic, are used in manufacturing of sweet commodity products. Alkaline isomerization of maltose gives *maltulose*, which is sweeter than maltose, while hydrogenation yields *maltitol* in a mixture with maltotriit. This mixture of sugar alcohols is not crystallizable but, after addition of suitable polysaccharides (alginate, methylcellulose), can be spray-dried into a powder.
Enzymatic transglucosylation of glucose syrup gives bifidogenic gentio-oligosaccharides. They consist of some glucose residues with a $\beta(1 \rightarrow 6)$ linkage.

#### 19.1.4.3.7 Polydextrose

When D-glucose is melted in the presence of small amounts of sorbitol and citric acid, a cross-linked polymer called polydextrose is formed, which contains primarily 1,6-glucosidic bonds but also other bonds. The caloric value is $\geq 4.2\,\mathrm{kJ/g}$. For this reason, the use of polydextrose as a sweetener for diabetics and for the production of low-calorie baked products and candies is under discussion.

### 19.1.4.4 Milk Sugar (Lactose) and Derived Products

#### 19.1.4.4.1 Milk Sugar

Lactose is produced from whey and its concentrates. The whey is adjusted to pH 4.7 and then heated directly with steam at 95–98 °C to remove milk albumins. The deproteinated filtered fluid is further concentrated in a multistage evaporator and then the separated salts are removed. The desalted concentrate yields a yellow raw sugar with a moisture content of 12–14%. The remaining mother liquor still contains an appreciable amount of lactose, so it is recirculated through the process or is used for the production of ethanol or lactic or propionic acids. The raw lactose is raffinated by solubilization, filtration and several crystallizations. The snow-white α-lactose monohydrate is pulverized in a pin mill and separated according to particle size in a centrifugal classifier. Spray drying of lactose is gaining in importance.
To increase lactose digestibility, sweetness and solubility, a 60% lactose solution can be heated to 93.5 °C and the crystallizate discharged to a vacuum drum dryer. β-Lactose (cf. 10.1.2.2) is formed. Its moisture content is not more than 1% and it is more soluble than α-lactose. Uses of β-lactose include: a nutrient for children; a filler or diluter in medicinal preparations (tablets); and an ingredient of nutrient solutions used in microbial production of antibiotics.

#### 19.1.4.4.2 Products from Lactose

Enzymatic or acidic hydrolysis of lactose provides a glucose-galactose mixture which is twice as sweet as lactose. A further increase in taste intensity is achieved by enzymatic isomerization of glucose. Such enzyme-treated products contain about 50% galactose, 29% glucose and 21% fructose.

*Lactulose* is obtained by the alkaline isomerization of lactose. It is sweeter than lactose. Hydrogenation of lactose yields *lactitol*, while hydrogenation of lactulose yields a mixture of lactilol and β-D-galactopyranosido-1,4-mannitol.
Bifidogenic galacto-oligosaccharides (α-D-Glu-(1 → 4)-[β-D-Gal-(1 → 6)-]$_n$, n = 2−5) and lactosucrose (β-D-Gal-(1 → 4)-α-D-Glu-(1 → 2)-β-D-Fru) are produced from lactose by transgalactosylation and transfructosylation (Table 19.1).

### 19.1.4.5 Fruit Sugar (Fructose)

Fructose is obtainable from its natural polymer, inulin, which occurs in: topinambur tubers (India) or its North American counterpart, Jerusalem artichoke (*Helianthus tuberosus*); chicory; tuberous roots of dahlia plants; and in flowerheads of globe or true artichoke (*Cyanara scolymus*), grown extensively in France. Fructose is obtained by acidic hydrolysis of inulin or by chromatographic separation of a glucose-fructose mixture (invert sugar, isomerized glucose syrup). Only the latter process has commercial significance. Fructose is present in the crystallized state as β-pyranose. Sweeter than sucrose, fructose is used as a sugar substitute for diabetics. It can be partly converted to glucose on boiling for longer periods due to the acid in fruit products.

### 19.1.4.6 L-Sorbose and Other L-Sugars

L-Sorbose can be formed from glucose via sorbitol. Sorbitol is oxidized by *Acetobacter xylium* into L-sorbose, an intermediary product for commercial synthesis of ascorbic acid (cf. 18.1.2.7). Sorbose is under discussion as a sucrose substitute for diabetics and as an ingredient with neglible cariogenicity in low calorie foods. It is resorbed only slowly on oral administration.
Until now, other L-sugars have been available only in small amounts. It is assumed that they are metabolized not at all or only to a small extent by human beings and even in low concentrations, they are capable of inhibiting the glycosidases of the small intestine. Therefore, economic methods of synthesis are of interest. A suitable educt is L-arabinose, which yields a L-glucose/L-mannose mixture by chain extension. This mixture can be oxidized directly to L-fructose or after reduction via L-sorbitol/L-mannitol. The isomerization of L-sorbose to L-idose and L-gulose is also under discussion.

### 19.1.4.7 Sugar Alcohols (Polyalcohols)

Sugar alcohols serve as sweetening agents for diabetics and are used as sugar substitutes in sugar-free candies and confectionery. Candies, bread and cakes contain these alcohols as moisturizers and softeners. Table 19.8 shows data on their use. Sugar alcohols have a low physiological calorific value.

#### 19.1.4.7.1 Isomaltol (Palatinit)

Palatinit is produced as described in 19.1.4.2. The sweetening strength of a 10% solution is 0.45 with reference to a 10% sucrose solution (sweet-

**Table 19.8.** Polyalcohols in candies, bread and cakes[a]

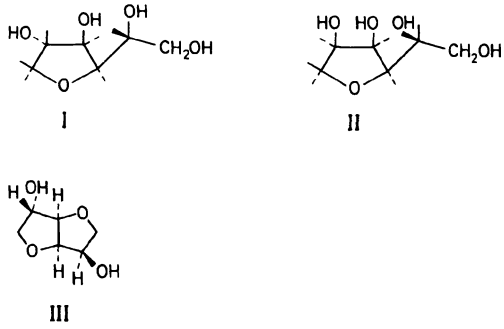
| Product | Sorbitol | Xylitol | Mannitol | Lactitol | Maltitol | Isomaltitol |
|---|---|---|---|---|---|---|
| Cake | 2.2–38.7 | – | 1.2–3.0 | – | 2.9–4.9 | – |
| Sugar-free confectionery | 342–864 | – | 23–41 | – | – | 487 |
| Confectionery | 1.5–101 | – | 1.4–1.7 | 0.9–2.7 | 5–360 | 165 |
| Chocolate | 2.9–19.5 | – | – | 53–122 | 46.5–109 | – |
| Chewing gum | 328–593 | 63.4–290 | 2.5–47.5 | – | 7.1–16.3 | – |

[a] Values in g/kg.

ening strength = 1.0). Palatinit is practically not hygroscopic.

19.1.4.7.2 Sorbitol

Sorbitol, a hygroscopic alcohol, is approximately half as sweet as sucrose. It is used as a sweetener for diabetics and in food canning. Sorbitol can be produced on a commercial scale by catalytic hydrogenation of glucose. Acid-catalyzed elimination of water yields a mixture of 1,4-sorbitan (85%, I) and 3,6-sorbitan (15%, II). Under more drastic conditions (action of concentrated acids), 1,4:3,6-dianhydrosorbitol (isosorbid III) is formed (Formula 19.2).




(19.2)

19.1.4.7.3 Xylitol

Xylose is obtained by hydrolysis of hemicelluloses. Catalytic hydrogenation of xylose yields xylitol. Xylitol is as sweet as sucrose. Due to its high heat of solution of $-23.27\,\mathrm{kJ/mol}$ (sucrose: $6.21\,\mathrm{kJ/mol}$), it produces a cooling effect in the mouth when it dissolves. This effect is utilized in some candies.

19.1.4.7.4 Mannitol

Mannitol can be made by the hydrogenation of invert sugar. As a result of its lower solubility, it is separated from sorbitol, which is also produced in the process, by chromatography.

## 19.1.5 Candies

### 19.1.5.1 General Outline

Candies represent a subgroup of sweet commodities generally called confectionery. Products such as long-storage cookies, cocoa and chocolate products, ice cream and invert sugar cream are also confections.

Candies are manufactured from all forms of sugar and may also incorporate other foods of diverse origin (dairy products, honey, fat, cocoa, chocolate, marmalade, jellies, fruit juices, herbs, spices, malt extract, seed kernels, rigid or elastic gels, liqueurs or spirits, essences, etc.). The essential and characteristic component of all types of candy is sugar, not only sucrose, but also other forms of sugar such as starch sugar, starch syrup, invert sugar, maltose, lactose, etc.

The important product groups include hard and soft caramels (bonbons, toffees), fondant, coconut flakes, foamy candies, gum candies, licorice products, dragees, pastilles, fruit pastes, chewing gum, croquant, effervescent powders, and products made of sugar and almonds, nuts and other protein-rich oil-containing seeds (marzipan, persipan, nougat).

### 19.1.5.2 Hard Caramel (Bonbons)

For the production of these candies, a sucrose solution is mixed with starch syrup and boiled down to the desired water content either batchwise or continuously (Fig. 19.10). Generally used are vacuum pans (120–160 °C) and film boiling machines in which evaporation takes place in a rotating cylinder (110 °C → 142 °C, 5 s). Volatile labile components (aroma substances) are added after cooling. This applies to acids as well in order to prevent inversion. Air is incorporated into the mass, if necessary. Subsequently, the mass is formed into a cord and processed into bonbons with the help of stamping or casting machines that require a slightly thinner mass. Modern plants have a capacity of 0.6–1.5 t/h.

The composition of hard caramels is presented in Table 19.9.

**Table 19.9.** Composition[a] of some candies

| Component | Hard caramel | Soft caramel | Fondant | Marzipan filler | Marzipan |
|---|---|---|---|---|---|
| Sucrose | 40–70 | 30–60 | 65–80[d] | ≤35 | ≤67.5 |
| Starch syrup[b] | 30–60 | 20–50 | 10–20 | 0 | 3.5 |
| Invert sugar | 1–8 | 1–10 | | 0–10 | 0–20 |
| Lactose | | 0–6 | | | |
| Sorbitol | | | | 0 | 0–5 |
| Fat | | 2–15 | | 28–33 | 14–16 |
| Acids[c] | 0.5–2 | | | | |
| Milk protein | | 0–5 | | | |
| Gelatin | | 0–0.5 | | | |
| Aroma | 0.1–0.3 | | | | |
| Water | 1–34 | 4–8 | 10–15 | 15–17 | 7–8.5 |
| Minerals | 0.1–0.2 | 0.5–1.5 | | 1.4–1.6 | 0.7–0.8 |

[a] Orientation values in %.
[b] Dry matter.
[c] Citric acid or tartaric acid.
[d] Glucose is also used, if necessary.

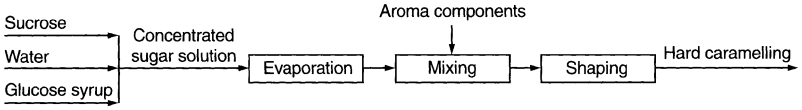



**Fig. 19.10.** Production of hard caramels

### 19.1.5.3 Soft Caramel (Toffees)

Milk, starch syrup, and fat are homogenized, mixed with sucrose solution, and boiled down as described above (cf. 19.1.5.2). Labile components are added after cooling. The fat content and, compared to hard caramel, slightly higher water content produce a plastic, partially elastic consistency, which is further improved by the incorporation of air in drawing machines. The mixing of powdered sugar or fondant filler during drawing produces a crumbly consistency due to partial sucrose crystallization. The cooled mass is formed into cords and cut.
The average composition is presented in Table 19.9.

### 19.1.5.4 Fondant

A sucrose or glucose solution is mixed with starch syrup and boiled down to a water content of 10–15%. The mass is rapidly cooled while it is subjected to intensive mechanical treatment. With partial crystallization (crystal diameter 3–30 mm), a dispersion of sucrose in a saturated sugar solution is formed. The mass solidifies on further cooling and is meltable and pourable on heating. It is aromatized and processed into various products, e. g., chocolate fillings.
The composition is presented in Table 19.9.

### 19.1.5.5 Foamy Candies

For the production of these candies, a hot sugar solution (sucrose/starch syrup) is carefully mixed into a stable protein foam (egg white, digested milk protein, gelatin). Apart from conventional beaters, pressure beaters are also used in which all the components are first mixed at 2–9 bar and then foamed by subsequent expansion. The light mass is shaped in a pressing step and possibly coated with chocolate.

#### 19.1.5.6 Jellies, Gum and Gelatine Candies

For the production of these products, an aromatized sugar solution is heated with polysaccharides (agar, pectin, gum arabic, thin-boiling starch, amylopectin) and gelatine, poured into starch moulds, and removed with powder after hardening. Typical products are jelly fruit and gum bears.

#### 19.1.5.7 Tablets

Powdered sugar and dextrose are aromatized, granulated with the addition of binding agents (fat, gelatine, gum arabic, tragacanth gum, starch) and lubricants (magnesium stearate), and tabletted under pressure.

#### 19.1.5.8 Dragées

The core (almond, nut, sugar crystal etc.) is moistened with a sugar solution in a rotating boiler and then covered with a layer of sugar by the subsequent addition of powdered sugar. This process is repeated until the desired layer thickness is attained. Chocolate, if necessary, is applied in a corresponding manner.
Sugared or burnt almonds are a well-known product. They consist of raw or roasted almonds which are covered with a hot-saturated and caramelized sugar syrup. The rough crispy surface is formed by the blowing of hot air. Burnt almonds also contain spice and flavoring matter, like vanillin etc. In a larger average sample, the ratio of sugar to almonds should not exceed 4:1. The sugar covering of burnt almonds produced in the dragée process can also be colored.

#### 19.1.5.9 Marzipan

In the traditional production of marzipan raw filler, sweet almonds are scalded, peeled on rubber-covered rolls, coarsely chopped, and then ground with the addition of not more than 35% of sucrose. The mixture is then roasted, e. g., in open roasting pans (95 °C; 45 min) or continually. After cooling, an equal amount of powdered sucrose is worked into this semi-finished product, possibly with the addition of starch syrup and/or sorbitol, to give the actual marzipan.
Almonds which contain the cyanogenic glycoside amygdalin (cf. 16.2.6) are scalded, peeled and then debittered by leaching with flowing water. The HCN content decreases by 80% in 24 h and the water content in the almonds increases to 38%. An extension of the process reduces the HCN content only slightly.
For reasons of rationalization and bacteriological stability, efforts are being made in modern processes to conduct all the process steps in one hermetically sealed reaction chamber, e. g., in a combined vacuum/boiling/cutting/mixing machine (high speed cooker), to prevent infections. After heating, partial drying occurs here by the application of vacuum. The cooker is aerated with germ-free filtered air. Koenigsberg marzipan is briefly baked on top after shaping. Marzipan potatoes are rolled in cocoa.

#### 19.1.5.10 Persipan

As with marzipan, a raw paste is initially prepared, but instead of almonds, the seed kernels of apricots, peaches or bitter almonds (with bitterness removed) are used. Commercial persipan is a mix of raw persipan filler and sucrose, the latter not more than half of the mix weight. Sucrose can be partially replaced by starch syrup and/or sorbitol.

#### 19.1.5.11 Other Raw Candy Fillers

These are produced from dehulled nuts such as cashews or peanuts. They correspond in composition to raw persipan paste. They are designated according to the oilseed component.

#### 19.1.5.12 Nougat Fillers

Nougat paste serves as a soft or firm candy filling. It contains up to 2% water and roasted dehulled filberts (hazelnuts) or roasted dehulled almonds, finely ground in the presence of sugar and cocoa products. Cocoa products

used are cocoa beans; cocoa liquor and butter; pulverized defatted cocoa; chocolate; baking, cream and milk chocolate; chocolate icing; cream and milk chocolate icings; and chocolate powders. The filler may contain a small amount of flavoring and/or lecithin. Also, part of the sugar may be replaced by cream or milk powder. Sweet nougat fillings can also be produced without cocoa ingredients and cream or milk powders. The kneaded nougat paste is often designated just as nougat or noisette.

Recently the trans- and cis-isomers of 5-methyl-4-hepten-2-one have been detected as character impact compounds for the flavor of filberts. The aroma threshold of the trans-isomer (Filbertone) is extremely low: 5 ng/kg (water as solvent).

Of special importance for the aroma of nougat is Filbertone, 5-methyl-(E)-2-hepten-3-one (odor threshold 5 ng/kg oil), which is produced during the roasting of hazelnuts. In a model experiment, the concentration of this compound increased at 180 °C from 1.4 to 660 μg/kg in 9 min and to 1150 μg/kg in 15 min. In fact, 315 μg/kg were found in a commercially produced oil from roasted nuts. Oil from unroasted nuts contains less than 10 μg/kg Filbertone.

#### 19.1.5.13 Croquant

Croquant serves generally as a filling for candy. It is made of molten sucrose, which has been at least partly caramelized, and ground and roasted almonds or nuts. It is occasionally mixed with marzipan, nougat, stable dairy products, fruit constituents and/or starch syrup. Croquant can be formulated to a brittle or soft consistency.

#### 19.1.5.14 Licorice and its Products

To manufacture licorice products, flour dough is mixed with sugar, starch syrup, concentrated flavoring of the licorice herb root and gelatin, and the mix is evaporated to a thick consistency. It is then molded into sticks, bands, figurines, etc. and dried further. The characteristic and flavor-determining ingredient derived from the perennial licorice herb is the diglucuronide of β-glycyrrhetinic acid (cf. 8.8.10).

Simple licorice products contain starch (30−45%), sucrose (30−40%) and at least 5% licorice extract. Better quality products have an extract content of at least 30%. The aroma is enhanced, usually, with anise seed oil in conjunction with low amounts of ammonium chloride.

#### 19.1.5.15 Chewing Gum

Chewing gum is made of a natural or a synthetic gum base impregnated with nutrients and flavoring constituents, mostly sugars and aroma substances, which are gradually released by chewing. The gum base is a blend of latex products from rubber trees that grow in tropical forests or plantations. The most important sources are chicle latex from the *Sapodilla* tree of Mexico, Indonesia and Malaysia; jelutongs; and rubber latex. Natural (mastic tree) and synthetic resins and waxes are also used. Synthetic thermoplastic resins are polyvinyl esters and ethers, polyethylene, polyisobutylene, butadiene-styrene copolymerisates, paraffin, microcrystalline waxes etc. The gum base may also contain cellulose as a filler and a break-up agent. The wax portion predominates in normal chewing gum and the gum-like substances predominate in bubble gum. To be able to process this base into a homogeneous plastic mass, it must be heated to ca. 60 °C before it is kneaded with the sugar components. The mass is made more malleable by the addition of small amounts of glycerol or glycerol triacetate. The mass is cooled to ca. 30 °C before it is rolled out. In fact, very strong kneaders must be used because of the high viscosity of the mass. Recently extruders have been used increasingly in continuous production lines. The production of chewing gum is summarized in Fig. 19.11.

#### 19.1.5.16 Effervescent Lemonade Powders

The powder or compressed tablets (effervescent bonbons) are used for preparation of artificial sparkling lemonades. They contain sodium bicarbonate and an acid component (lactic, tartaric or citric acid). When dissolved in water, they generate carbon dioxide. Other constituents of the product are sucrose or another sweetener, and nat-

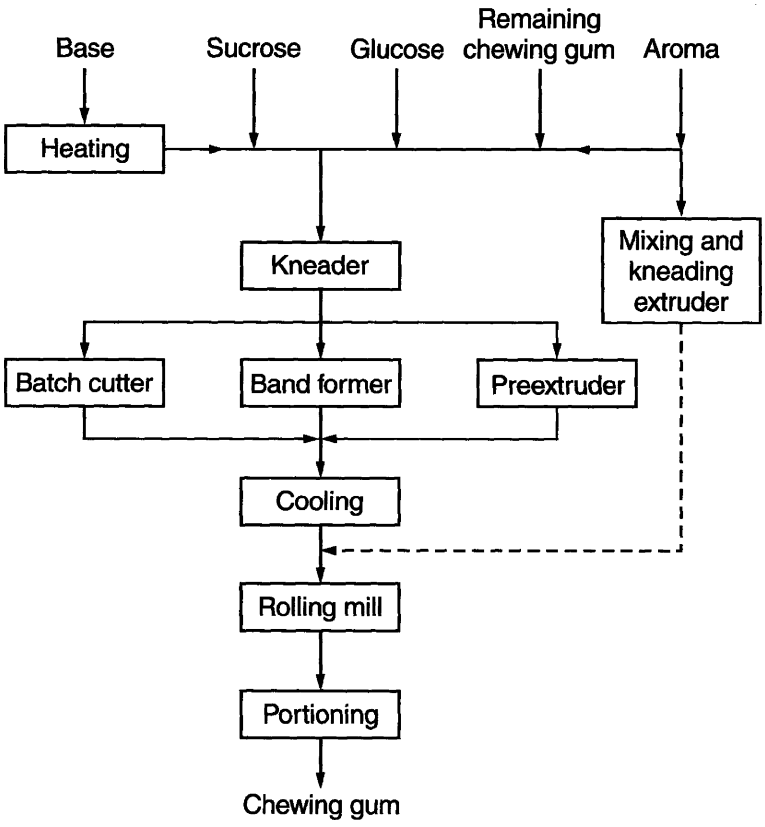



**Fig. 19.11.** Production of chewing gum

ural or artificial flavoring substances. Sodium bicarbonate and acids are often packaged and marketed separately in individual capsules or in two separate containers.

## 19.2 Honey and Artificial Honey

### 19.2.1 Honey

#### 19.2.1.1 Foreword

Honey is produced by honeybees. They suck up nectar from flowers or other sweet saps found in living plants, store the nectar in their honey sac, and enrich it with some of their own substances to induce changes. When the bees return to the hive, they deposit the nectar in honeycombs for storage and ripening.

Honey production starts immediately after the flower pollen, nectar and honeydew are collected and deposited in the bee's pouch (honey sac). The mixture of raw materials is then given to worker bees in the hive to deposit it in the six-sided individual cells of the honeycomb. The changing of nectar into honey proceeds in the cell in the following stages: water evaporates from the nectar, which then thickens; the content of invert sugar increases through sucrose hydrolysis by acids and enzymes derived from bees, while an additional isomerization of glucose to fructose occurs in the honey sac; absorption of proteins from plant and bees, and acids from the bee's body; assimilation of forage minerals, vitamins and aroma substances; and absorption of enzymes from the bees' salivary glands and honey sacs. When the water content of the honey drops to 16–19%, the cells are closed with a wax lid and ripening continues, as reflected by a continued

hydrolysis of sucrose by the enzyme invertase and by the synthesis of new sugars.

#### 19.2.1.2 Production and Types

In the production and processing of honey, it is important to preserve the original composition, particularly the content of aroma substances, and to avoid contamination. The following kinds of honey are differentiated according to recovery techniques:

*Comb Honey* (honey with waxy cells), i. e. honey present in freshly-built, closed combs devoid of brood combs (young virgin combs). Such honey is produced in high amounts, but is not readily found in Germany. In other countries, primarily the USA, Canada and Mexico, it is widely available. Darker colored honey is obtained from covered virgin combs not more than one year old and from combs which include those used as brood combs.

*Extracted Honey* is obtained with a honey extractor, i. e. by centrifugation at somewhat elevated temperatures of brood-free comb cells. This recovery technique provides the bulk of the honey found on the market. Gentle warming up to 40 °C facilitates the release of honey from the combs.

*Pressed Honey* is collected by compressing the brood-free honey combs in a hydraulic press at room temperature.

*Strained Honey* is collected from brood-free, pulped or unpulped honey combs by gentle heating followed by pressing.

*Beetle Honey* is recovered by pulping honey combs which include brood combs. This type of honey is used only for feeding bees.

Based on its use, honey is distinguished as:

*Honey for Domestic use.* This is the highest quality product, and is consumed and enjoyed in pure form.

*Baking Honey.* This type of honey is not of high quality and is used in place of sugar in the baking industry. Such honey has spontaneously fermented, to a certain degree has absorbed or acquired other foreign odors and flavors, or was overheated. This category includes caramelized honey.

According to the recovery (harvest) time, honey is characterized as: early (collected until the end of May); main (June and July); and late (August and September).

Honey can be classified according to geographical origin, e. g., German (Black Forest or Allgäu honey), Hungarian, Californian, Canadian, Chilean, Havanan, etc.

The flavor and color of honey are influenced by the kinds of flowers from which the nectar originates. The following kinds of honey are classified on the basis of the type of plant from which they are obtained.

*Flower Honey,* e. g., from: heather; linden; acacia; alsike, sweet and white clovers; alfalfa; rape; buckwheat and fruit tree blossoms. When freshly manufactured, these are thick, transparent liquids which gradually granulate by developing sugar crystals. Flower honey is white, light-to-dark, greenish-yellow or brownish. Maple tree honey is light amber; alfalfa honey, dark-red; clover honey, light amber-to-reddish; and meadow flower honey, amber-to-brown. Flower honey has a typical sweet and highly aromatic flavor that is dependent on the flavor substances which together with the nectar are collected by the bees; it sometimes has a flavor reminiscent of molasses. This is especially true of honey derived from heather (alfalfa and buckwheat honeys).

*Honeydew Honey* (pine, spruce or leaf honeydew). This type of honey solidifies with difficulty. It is less sweet, dark colored, and may often have a resinous terpene-like odor and flavor.

#### 19.2.1.3 Processing

Honey is marketed as a liquid or semisolid product.

It is usually oversaturated with glucose, which granulates, i. e. crystallizes, within the thick syrup in the form of glucose hydrate. To stabilize liquid honey, it has to be filtered under pressure to remove the sugar crystals and other crystallization seeds. Heating of honey decreases its viscosity during processing and filling, and provides complete glucose solubilization and pasteurization. Heating has to be gentle since the low pH of

honey and its high fructose content make it sensitive to heat treatment. As with other foods, continuous, high temperature-short time processing (e. g., 65 °C for 30 s followed by rapid cooling) is advantageous.
Processing of honey into a semisolid product involves seeding of liquid honey with fine crystalline honey to 10% and storing for one week at 14 °C to allow full crystallization. This product is marketed as creamed honey.

#### 19.2.1.4 Physical Properties

Honey density (at 20 °C) depends on the water content and may range from 1.4404 (14% water) to 1.3550 (21% water). Honey is hygroscopic and hence is kept in airtight containers. Viscosity data at various temperatures are given in Table 19.10. Most honeys behave like *Newtonian* fluids. Some, however, such as alfalfa honey, show thixotropic properties which are traceable to the presence of proteins, or dilating properties (as with opuntia cactus honey) due to the presence of trace amounts of dextran.

#### 19.2.1.5 Composition

Honey is essentially a concentrated aqueous solution of invert sugar, but it also contains a very complex mixture of other carbohydrates, several enzymes, amino and organic acids, minerals, aroma substances, pigments, waxes, pollen grains, etc. Table 19.11 provides compositional data. The analytical data correspond to honey from the USA, nevertheless, they basically represent the composition of honey from other countries.

**Table 19.10.** Viscosity of honey at various temperatures

| | Temperature (°C) | Viscosity (Poise) |
|---|---|---|
| Honey 1[a] | 13.7 | 600.0 |
| | 20.6 | 189.6 |
| | 29.0 | 68.4 |
| | 39.4 | 21.4 |
| | 48.1 | 10.7 |
| | 71.1 | 2.6 |
| Honey 2[b] | 11.7 | 729.6 |
| | 20.2 | 184.8 |
| | 30.7 | 55.2 |
| | 40.9 | 19.2 |
| | 50.7 | 9.5 |

[a] Melilot honey (*Melilotus officinalis*; 16.1% moisture).
[b] Sage honey (*Salvia officinalis*; moisture content 18.6%).

**Table 19.11.** Composition of honey (%)

| Constituent | Average value | Variation range |
|---|---|---|
| Moisture | 17.2 | 13.4–22.9 |
| Fructose | 38.2 | 27.3–44.3 |
| Glucose | 31.3 | 22.0–40.8 |
| Saccharose | 2.4 | 1.7–3.0 |
| Maltose | 7.3 | 2.7–16.0 |
| Higher sugars | 1.5 | 0.1–8.5 |
| Others | 3.1 | 0–13.2 |
| Nitrogen | 0.06 | 0.05–0.08 |
| Minerals (ash) | 0.22 | 0.20–0.24 |
| Free acids[a] | 22 | 6.8–47.2 |
| Lactones[a] | 7.1 | 0–18.8 |
| Total acids[a] | 29.1 | 8.7–59.5 |
| pH value | 3.9 | 3.4–6.1 |
| Diastase value | 20.8 | 2.1–61.2 |

[a] mequivalent/kg.

##### 19.2.1.5.1 Water

The water content of honey should be less than 20%. Honey with higher water content is readily susceptible to fermentation by osmophilic yeasts. Yeast fermentation is negligible when the water contents is less than 17.1%, while between 17.1 and 20% fermentation depends on the count of osmophilic yeast buds.

##### 19.2.1.5.2 Carbohydrates

Fructose (averaging 38%) and glucose (averaging 31%) are the predominant sugars in honey. Other monosaccharides have not been found. However, more than 20 di- and oligosaccharides have been identified (Table 19.12), with maltose predominating, followed by kojibiose (Table 19.13). The composition of disaccharides depends largely on

**Table 19.12.** Sugars identified in honey

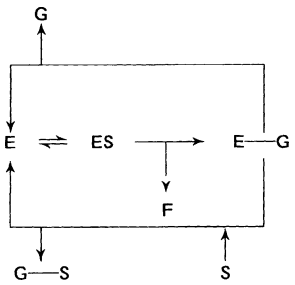
| Common name | Systematic name |
|---|---|
| Glucose | |
| Fructose | |
| Saccharose | α-D-glucopyranosyl-β-D-fructo-furanoside |
| Maltose | O-α-D-glucopyranosyl-(1 → 4)-D-glucopyranose |
| Isomaltose | O-α-D-glucopyranosyl-(1 → 6)-D-glucopyranose |
| Maltulose | O-α-D-glucopyranosyl-(1 → 4)-D-fructose |
| Nigerose | O-α-D-glucopyranosyl-(1 → 3)- D-glucopyranose |
| Turanose | O-α-D-glucopyranosyl-(1 → 3)-D-fructose |
| Kojibiose | O-α-D-glucopyranosyl-(1 → 2)-D-glucopyranose |
| Laminaribiose | O-β-D-glucopyranosyl-(1 → 3)-D-glucopyranose |
| α, β-Trehalose | α-D-glucopyranosyl-β-D-glucopyranoside |
| Gentiobiose | O-β-D-glucopyranosyl-(1 → 6)-D-glucopyranose |
| Melezitose | O-β-D-glucopyranosyl-(1 → 3)-O-β-D-fructofuranosyl-(2 → 1)-α-D-glucopyranoside |
| 3-α-Isomaltosylglucose | O-α-D-glucopyranosyl-(1 → 6)-O-α-D-glucopyranosyl-(1 → 3)-D-glucopyranose |
| Maltotriose | O-α-D-glucopyranosyl-(1 → 4)-O-α-D-glucopyranosyl-(1 → 4)-D-gluco-pyranose |
| 1-Kestose | O-α-D-glucopyranosyl-(1 → 2)-β-D-α-fructofuranosyl-(1 → 2)-β-D-fructofuranoside |
| Panose | O-α-D-glucopyranosyl-(1 → 6)-O-α-D-glucopyranosyl-(1 → 4)-D-glucopyranose |
| Isomaltotriose | O-α-D-glucopyranosyl-(1 → 6)-O-α-D-glucopyranosyl-(1 → 6)-D-glucopyranose |
| Erlose | O-α-D-glucopyranosyl-(1 → 4)-α-D-glucopyranosyl-β-D-fructofuranoside |
| Theanderose | O-α-D-glucopyranosyl-(1 → 6)-α-D-glucopyranosyl-β-D-fructofuranoside |
| Centose | O-α-D-glucopyranosyl-(1 → 4)-O-α-D-glucopyranosyl-(1 → 2)-D-glucopyranose |
| Isopanose | O-α-D-glucopyranosyl-(1 → 4)-O-α-D-glucopyranosyl-(1 → 6)-D-gluco-pyranose |
| Isomaltotetraose | O-α-D-glucopyranosyl-(1 → 6)-[O-α-D-glucopyranosyl-(1 → 6)]$_2$-D-gluco-pyranose |
| Isomaltopentaose | O-α-D-glucopyranosyl-(1 → 6)-[O-α-D-glucopyranosyl-(1 → 6)]$_3$-D-gluco-pyranose |

the plants from which the honey was derived, while geographical and seasonal effects are negligible. The content of sucrose varies appreciably with the honey ripening stage.

#### 19.2.1.5.3 Enzymes

The most prominent enzymes in honey are α-glucosidase(invertase or saccharase), α- and β-amylases (diastase), glucose oxidase, catalase and acid phosphatase. Average enzyme activities are presented in Table 19.14. Invertase and diastase activities, together with the hydroxymethyl furfural content, are of significance for assessing whether or not the honey was heated.

For α-glucosidase, 7−18 isoenzymes are known. In a wide pH optimum between 5.8−6.5 the enzyme hydrolyzes maltose and other α-glucosides. The $K_M$ with sucrose as substrate is 0.030 mol/l. It also possesses transglucosylase activity. During the first stage of sucrose hydrolysis the trisaccharide erlose (α-maltosyl-β-D-fructofuranoside) plus other oligosaccharides are formed (E = enzyme, S = sucrose, G = glucose, F = fructose):




(19.3)

As the hydrolysis proceeds, most of these oligosaccharides are cleaved into monosaccharides.

Thermal inactivation of invertase in honey and its half-life values at various temperatures have been thoroughly investigated. These data are presented in Figs. 19.12 and 19.13. Practically all invertase activity is derived from bees.

Honey α- and β-*amylases (diastase)* also originate from bees. Their pH optimum range

**Table 19.13.** Oligosaccharide composition of honey

| Sugar | Content[a] (%) |
|---|---|
| *Disaccharides* | |
| Maltose | 29.4 |
| Kojibiose | 8.2 |
| Turanose | 4.7 |
| Isomaltose | 4.4 |
| Saccharose | 3.9 |
| Maltulose (and two unidentified ketoses) | 3.1 |
| Nigerose | 1.7 |
| α-, β-Trehalose | 1.1 |
| Gentiobiose | 0.4 |
| Laminaribiose | 0.09 |
| *Trisaccharides* | |
| Erlose | 4.5 |
| Theanderose | 2.7 |
| Panose | 2.5 |
| Maltotriose | 1.9 |
| 1-Kestose | 0.9 |
| Isomaltotriose | 0.6 |
| Melezitose | 0.3 |
| Isopanose | 0.24 |
| Gentose | 0.05 |
| 3-α-Isomaltosylglucose | +[b] |
| *Higher Oligosaccharides* | |
| Isomaltotetraose | 0.33 |
| Isomaltopentaose | 0.16 |
| *Acidic fraction* | 6.51 |

[a] Values are based on oligosaccharide total content (= 100%) which in honey averages 3.65%. Only the most important sugars are presented.
[b] Traces.

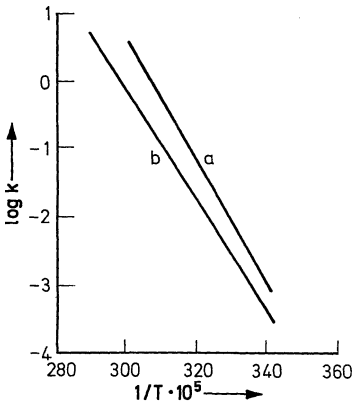



**Fig. 19.12.** Inactivation rate of (a) invertase and (b) diastase in honey (according to *White*, 1978)

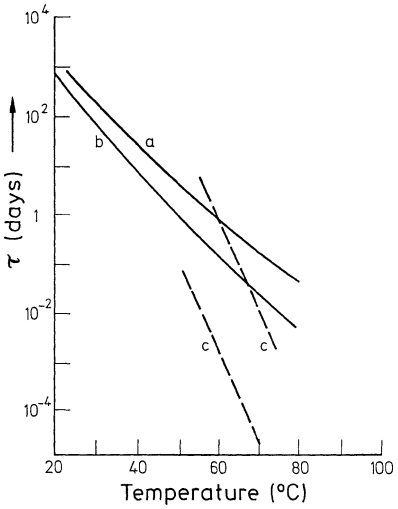



**Fig. 19.13.** Half-life activity ("$\tau$") of diastase (a), invertase (b), and glucose oxidase (c) in honey at various temperatures (according to *White*, 1978)

**Table 19.14.** Average enzyme activity in honey

| Number | Enzyme | Activity[a] |
|---|---|---|
| 1 | α-Glucosidase (saccharase) | 7.5–10 |
| 2 | Diastase (α- and β-amylase) | 16–24 |
| 3 | Glucose oxidase | 80.8–210 |
| 4 | Catalase | 0–86.8 |
| 5 | Acid phosphatase | 5.07–13.4 |

[a] **1**: g saccharose hydrolyzed by 100 g honey per hour at 40 °C; **2**: g starch degraded by 100 g honey per hour at 40 °C; **3**: μg $H_2O_2$ formed per g honey/h; **4**: catalytic activity/g honey, and **5**: mg P/100 g honey released in 24 h.

is 5.0–5.3. Diastase activity is somewhat more thermally stable than invertase activity (Figs. 19.12 and 19.13).

*Glucose oxidase* presence in honey is also derived from bees. Its optimum pH is 6.1. The enzyme oxidizes glucose (100%) and mannose (9%). The enzymatic oxidation by-product, hydrogen peroxide, is partly responsible for a bacteriostatic effect of nonheated honey, an effect earlier ascribed to a so-called "inhibine". The enzymatic oxidation yields gluconic acid, the main acid in honey. Glucose oxidase activity and thermal stability in honey vary widely (limit values were given in Ta-

ble 19.13), hence this enzyme is not a suitable indicator of the thermally treatment of honey.

*Catalase* in honey most probably originates from pollen which, unlike flower nectar, has a high activity of this enzyme. Similarly, honey *acid phosphatase* originates mainly from pollen, although some activity comes from flower nectars.

#### 19.2.1.5.4 Proteins

Honey proteins are derived partly from plants and partly from honeybees. Figure 19.14 shows that bees fed on sucrose provide proteins with less complex patterns than, for example, cottonflower honey.

#### 19.2.1.5.5 Amino Acids

Honey contains free amino acids at a level of 100 mg/100 g solids. Proline, which might originate from bees, is the prevalent amino acid and is 50–85% of the amino acid fraction (Table 19.15). Based on several amino acid ratios, it is possible to identify the geographical or regional origin of honeys (Fig. 19.15).

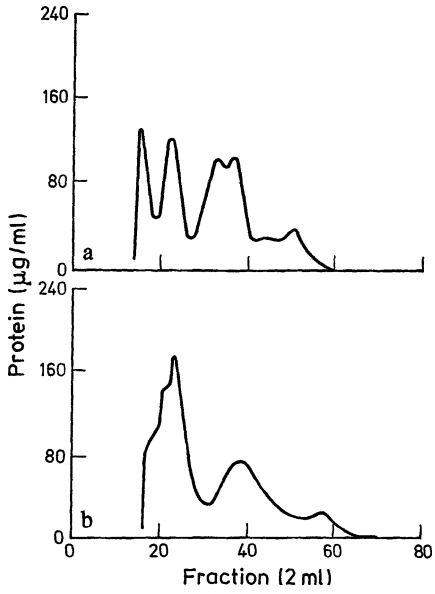



**Fig. 19.14.** Protein profiles of two honey varieties as revealed by gel filtration on Sephadex G-200. (a) Cottonflower honey (b), honey from sugar-fed bees (according to *White*, 1978)

**Table 19.15.** Free amino acids in honey

| Amino acid | mg/100 g honey (dry weight basis) | Amino acid | mg/100 g honey (dry weight basis) |
|---|---|---|---|
| Asp | 3.44 | Tyr | 2.58 |
| Asn + Gln | 11.64 | Phe | 14.75 |
| Glu | 2.94 | β-Ala | 1.06 |
| Pro | 59.65 | γ-Abu | 2.15 |
| Gly | 0.68 | Lys | 0.99 |
| Ala | 2.07 | Orn | 0.26 |
| Cys | 0.47 | His | 3.84 |
| Val | 2.00 | Trp | 3.84 |
| Met | 0.33 | Unidentified | |
| Met-O | 1.74 | AA′s (6) | 24.53 |
| Ile | 1.12 | | |
| Leu | 1.03 | | |
| Arg | 1.72 | | |
| | | Total | 118.77 |

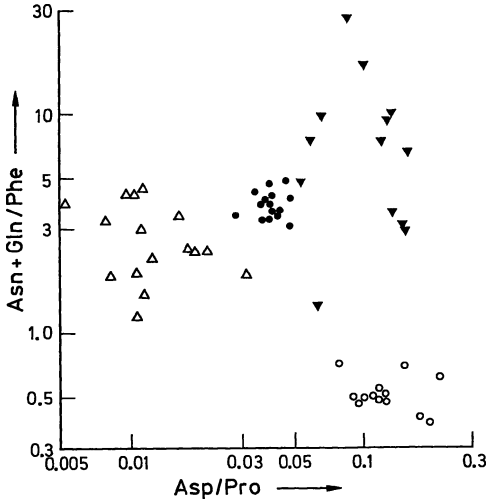



**Fig. 19.15.** Regional origin of honey as related to its amino acid composition. (according to *White*, 1978) Honey origin: △ Australia, ● Canada, ▼ United States (clover), ○ Yucatan

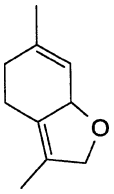
#### 19.2.1.5.6 Acids

The principal organic acid in honey is gluconic acid, which results from glucose oxidase activity.

In honey gluconic acid is in equilibrium with its gluconolactone. The acid level is mostly dependent on the time elapsed between nectar collection by bees and achievement of the final honey density in honeycomb cells. Glucose oxidase activity drops to a negligible level in thickened honey. Other acids present in honey only in small amounts are: acetic, butyric, lactic, citric, succinic, formic, maleic, malic and oxalic acids.

#### 19.2.1.5.7 Aroma Substances

About 300 volatile compounds are present in honey and more than 200 have been identified. There are esters of aliphatic and aromatic acids, aldehydes, ketones and alcohols. Of importance are especially β-damascenone and phenylacetaldehyde, which have a honey-like odor and taste. Methyl anthranilate is typical of the honey from citrus varieties and lavender and 2,4,5,7a-tetrahydro-3, 6-dimethylbenzofuran (Formula 19.4, linden ether) is typical of linden honey.



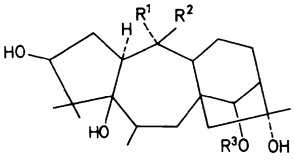

(19.4)

#### 19.2.1.5.8 Pigments

Relatively little is known about honey color pigments. The amber color appears to originate from phenolic compounds and from products of the nonenzymic browning reactions between amino acids and fructose.

#### 19.2.1.5.9 Toxic Constituents

Poisonous honey (pontius or insane honey) has been known since the time of the Greek historian and general, *Xenophon*, and the Roman writer, *Plinius*. It comes mostly from bees collecting their nectar from: rhododendron species (Asia Minor, Caucasus Mountains); some plants of the family *Ericacea*; insane ("mad") berries; *Kalmia* evergreen shrubs; *Eurphorbiaceae*; and honey collected from other sweet substances, e. g., honeydew exudates of grasshoppers. Rhododendrons contain the poisonous compounds, andromedotoxin (an acetylandromedol) and grayanotoxins I, II and III (a tetra-cyclic diterpene) used in medicine as a muscle relaxant (I: $R^1$ = OH, $R^2 = CH_3$, $R^3 = COCH_3$; II: $R^1$, $R^2 = CH_2$, $R^3$ = H; III: $R^1$ = OH, $R^2 = CH_3$, $R^3$ = H) (see Formula 19.5).




(19.5)

The poisonous nature of New Zealand honey is a result of tutin and hyenanchin (mellitoxin) toxins from the tutu shrub (tanner shrub plant, *Coriaria arbora*). Poisonous flowers of tobacco, oleander, jasmine, henbane (*Datura metel*) and of hemlock (*Conium maculatum*) provide nonpoisonous honeys. The production of these honeys is negligible in Europe.

### 19.2.1.6 Storage

Honey color generally darkens on storage, the aroma intensity decreases and the content of hydroxymethyl furfural increases, depending on pH,

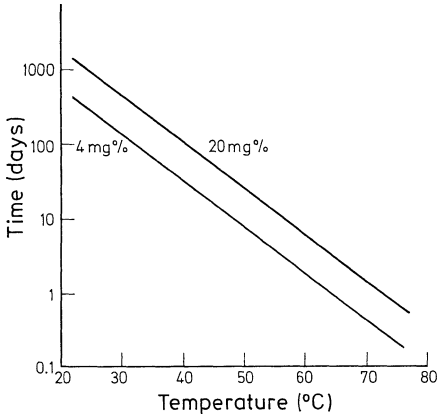



**Fig. 19.16.** Hydroxymethyl furfural formation in honey versus temperature and time (according to *White*, 1978)

storage time and temperature (Fig. 19.16). The enzymatic inversion of sucrose also continues at a low level even when honey has reached its final density.
Honey should be protected from air moisture and kept at temperatures lower than 10 °C when stored. The desired temperature range for use is 18 – 24 °C.

#### 19.2.1.7 Utilization

Honey use goes back to prehistoric times. Beeswax and honey played an important role in ancient civilizations. They were placed into tombs as food for deceased spirits, while the Old Testament describes the promised land as "a land flowing with milk and honey". In the Middle Ages honey was used as an excellent energy food and, up to the introduction of cane sugar, served as the only food sweetener. Besides being enjoyed as honey, it is used in baking (honey cookies, etc.) or in the manufacturing of alcoholic beverages by mixing with alcohol (honey liqueur, "beartrag") or by fermentation into honey flavored wine (Met). Preparations containing honey, in combination with milk and cereals, are processed for children. Tobacco products are occasionally flavored with honey. In medicine, honey is used in pure form or prescribed in preparations such as honey milk, fennel honey and ointments for wounds. It is incorporated into cosmetics in glycerol-honey gels and tanning cream products. The importance of honey as a food and as a nutrient is based primarily on its aroma constituents and the high content and fast absorption of its carbohydrates.

### 19.2.2 Artificial Honey

#### 19.2.2.1 Foreword

Artificial honey is mostly inverted sucrose from beet or cane sugar and is produced with or without starch sugar or starch syrup. It is adjusted in appearance, odor and flavor to imitate true honey. Depending on the production method, such creams contain nonsugar constituents, minerals, sucrose and hydroxymethyl furfural.

#### 19.2.2.2 Production

Sucrose (75% solution) is cleaved into glucose and fructose by acidic hydrolysis using hydrochloric, sulfuric, phosphoric, carbonic, formic, lactic, tartaric or citric acid or, less frequently, enzymatically using invertase. The acid used for inversion is then neutralized with sodium carbonate or bicarbonate, calcium carbonate, etc. The inverted sugar is then aromatized, occasionally with strongly flavored natural honey. To facilitate crystallization, it is seeded with an invert sugar mixture that has already solidified, then packaged with automated machines. During inversion, an oligosaccharide (a "reversion dextrin") is also formed, mostly from fructose. Overinversion by prolonged heating results in dark coloring of the product and in some bitter flavor. Moreover, glucose and fructose degradation forms a noticeable level of hydroxymethyl furfural – this could be used for identification of artificial honey.
Liquid artificial honey is made from inverted and neutralized sucrose syrup. To prevent crystallization, up to 20% of a mildly degraded, dextrin-enriched starch syrup is added (the amount added is proportional to the end-product weight).

#### 19.2.2.3 Composition

Artificial honey contains invert sugar ($\geq$50%), sucrose ($\leq$38.5%) water ($\leq$22%), ash ($\leq$0.5%) and, when necessary, saccharified starch products ($\leq$38.5%). The pH of the mixture should be $\geq$2.5. The aroma carrier is primarily phenylacetic acid ethyl ester and, occasionally, diacetyl, etc. Hydroxymethyl furfural content is 0.08−0.14%. The product is often colored with certified food colors.

#### 19.2.2.4 Utilization

Artificial honey is used as a sweet spread for bread and for making Printen (honey cookies covered with almonds), gingerbread and other baked products.

## 19.3 References[a]


Birch, G.G., Green, L.F. (Eds.): Molecular structure and function of food carbohydrates. Applied Science Publ.: London. 1973

Blank, I., Fischer, K.-H., Grosch, W.: Intensive neutral odorants of linden honey. – Differences from honeys of other botanical origin. Z. Lebensm. Unters. Forsch. *189*, 426 (1989)

Crane, E. (Ed.): Honey. Heinemann. London. 1979

Crittenden, R.G., Playne, M.J.: Production, properties and applications of food-grade oligosaccharides. Trends Food Sci. Technol. *7*, 353 (1996)

Fincke, A.: Zuckerwaren. In: Ullmanns Encyklopädie der technischen Chemie, 4. edn., Vol. 24, p. 795, Verlag Chemie: Weinheim. 1983

Hoffmann, H., Mauch, W., Untze, W.: Zucker und Zuckerwaren. Verlag Paul Parey: Berlin. 1985

Hough, C.A.M., Parker, K.J.; Vlitos, A.J. (Eds.): Developments in sweeteners-1 ff. Applied Science Publ.: London. 1979 ff

Jeanes, A., Hodge, J. (Eds.): Physiological effects of food carbohydrates. ACS Symposium Series 15, American Chemical Society: Washington, D.C. 1975

Katan, M.B., DeRoos, N.: Promises and problems of functional foods. Crit. Rev. Food Sci. Nutr. *44*, 369 (2004)

Koivistoinen, P., Hyvönen, L. (Eds.): Carbohydrate sweeteners in foods and nutrition. Academic Press: New York. 1980

Lehmann, J., Tegge, G., Huchette, M., Pritzwald-Stegmann, B.F., Reiff, F., Raunhardt, O., Van Velthuysen, J.A., Schiweck, H., Schulz, G.: Zucker, Zuckeralkohole und Gluconsäure. In: Ullmanns Encyklopädie der technischen Chemie, 4. edn., Vol. 24, p. 749, Verlag Chemie: Weinheim. 1983

Pancoast, H.M., Junk, W.R.: Handbook of sugars, 2nd edn., AVI Publ. Co.: Westport, Conn. 1980

Pfnuer, P., Matsui, T., Grosch, W., Guth, H., Hofmann, T., Schieberle, P.: Development of a stable isotope dilution assay for the quantification of 5-methyl-(E)-2-hepten-4-one: Application to hazelnut oils and hazelnuts. J. Agric. Food Chem. *47*, 2044 (1999)

Quax, W.J.: Thermostable glucose isomerases. Trends Food Sci. Technol. *4*, 31 (1993)

Rymon Lipinski, G.-W. von, Schiweck, H.: Handbuch Süßungsmittel. Behr's Verlag: Hamburg. 1991

Schiweck, H.: Disaccharidalkohole. Süßwaren *22* (14), 13 (1978)

Schiweck, H., Clarke, M.: Sugar. In: Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, Volume A25, p. 345, Verlag Chemie, Weinheim, 1994

Schiweck, H., Bär, A., Vogel, R., Schwarz, E., Kunz, M.: Sugar alcohols. In: Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, Volume A25, p. 413, Verlag Chemie, Weinheim, 1994

Shallenberger, R.S., Birch, G.G.: Sugar chemistry. AVI Publ. Co.: Westport, Conn. 1975

Sturm, W., Hanssen, E.: Über Cyanwasserstoff in Prunoideensamen und einigen anderen Lebensmitteln. Z. Lebensm. Unters. Forsch. *135*, 249 (1967)

Tegge, G., Riehm, T., Sinner, M., Puls, J., Sahm, H.: Verzuckerung von Stärke und cellulosehaltigen Materialien. In: Ullmanns Encyklopädie der technischen Chemie, 4. edn., Vol. 23, p. 555, Verlag Chemie: Weinheim. 1983

White jr., J.W.: Honey. Adv. Food Res. *24*, 287 (1978)


[a] cf. 4.5